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LXXXVII.—ACTION OF SODIC ALCOHOLATES ON CHLORANIL. ACETALS DERIVED FROM SUBSTITUTED QUINONES.[1]

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[*Continued from page 607.*]

Dichlordiethoxyquinone Tetraethylacetal,

$C_6Cl_2(OC_2H_5)_2(OC_2H_5)_4$.

It has already been stated that ethyl or methyl iodide did not act on either the free hemiacetal or its sodium salt; if, however, the silver salt of dichlordiethoxyquinone diethylhemiacetal was treated with ethyl iodide, the corresponding tetraethylacetal was formed. As this compound could be obtained only in very small quantities and with great difficulty, it was necessary to prepare the sodium and silver salts of the hemiacetal on a large scale, which was done as follows: 40 grams of dichlordiphenoxyquinone were mixed with the sodic ethylate made by treating 10 grams of metallic sodium with 150 cc. of absolute alcohol, and in order to complete the reaction the mixture was warmed on the steam-bath for a few minutes, and then allowed to stand at ordinary temperatures for four or five hours. The sodium salt of the dichlordiethoxyquinone diethylhemiacetal, which separated in large amount, was fil-

[1] Presented to the American Academy of Arts and Sciences, May 9, 1894.

tered off, and washed thoroughly, first with a mixture consisting of equal parts of alcohol and ether, and finally with ether alone. In this way 40–42 grams of the essentially pure sodium salt were obtained instead of the 44 grams required by the theory; the yield, therefore, was between 90 and 95 per cent. of the theoretical.

In order to prepare the silver salt of the diethylhemiacetal, a concentrated aqueous solution of the sodium salt was treated with 25 grams of argentic nitrate dissolved in a small amount of water. The insoluble silver salt was filtered, washed thoroughly with water, alcohol, and ether, and then dried as quickly as possible by sucking a stream of air through it with the filter-pump.

The silver salt of the dichlordiethoxyquinone diethylhemi acetal was then suspended in ether, and treated in the cold with ethyl iodide, when, in addition to a very small quantity of the tetraethylacetal, a large amount of dichlordiethoxyquinone was obtained. The acetal was separated from the quinone by treating the products of the reaction with a dilute solution of sodic hydrate in 50-per cent. alcohol, which converted the dichlordiethoxyquinone into the sodium salt of chloranilic acid, while the dichlordiethoxyquinone tetraethylacetal was not affected by it. By washing with water it was then easy to separate the freely soluble sodic chloranilate from the insoluble acetal, which was purified by recrystallization from ligroïn until it showed the constant melting-point 101°–102°, when it was dried in a desiccator, and on analysis gave the following results:

I. 0.2039 gram substance gave on combustion 0.3928 gram CO_2 and 0.1335 gram H_2O.

II. 0.2177 gram substance gave on combustion 0.4181 gram CO_2. The water determination was lost.

III. 0.1843 gram substance gave 0.1304 gram AgCl (Carius).

IV. 0.1620 gram substance gave 0.1135 gram AgCl.

	Calculated for $C_6Cl_2(OC_2H_5)_2(OC_2H_5)_4$.	Found. I.	II.	III.	IV.
Carbon	52.30	52.54	52.37	....	....
Hydrogen	7.26	7.28	....	....	....
Chlorine	17.19	....	....	17.49	17.32

The yield, as has been already stated, is very small.

Properties of Dichlordiethoxyquinone Tetraethylacetal.—This substance can be obtained from ligroïn in good-sized white rhombic prisms, but when more rapidly crystallized it forms irregularly fan-shaped groups of very much branched needles resembling certain delicate seaweeds, or four-sided plates nearly but not quite rectangular and much striated. It melts at 101°–102°. By heating in a capillary tube it is apparently not decomposed even at so high a temperature as 275°, but between 260° and 275° it sublimes, giving beautiful white crystals in the upper part of the tube. It is very easily soluble in ether, benzol, alcohol, chloroform, acetone, ligroïn, glacial acetic acid, carbonic disulphide, acetic anhydride, or methyl alcohol, but is insoluble in water. Ligroïn is the best solvent for it.

It is saponified by sulphuric acid of specific gravity 1.44, giving the dichlordiethoxyquinone melting at 104–105°, and also a small quantity of chloranilic acid. In the cold the acid produces little or no effect on the acetal, but after warming on the steam-bath for half an hour the saponification is complete. A more dilute acid seems to have no action upon it. Sodic hydrate, even when boiling or mixed with alcohol, does not decompose the acetal.

The differences between the properties of the tetraethylacetal and the diethylhemiacetal certainly are remarkable. The hemiacetal is entirely insoluble, while the acetal is exceedingly soluble in all the common solvents except water. The former is very unstable, being readily decomposed by even very dilute acids, while the latter is saponified only slowly by comparatively strong acids when heated with them. By heat also the hemiacetal is easily decomposed, whereas the acetal sublimes apparently unaltered at high temperatures.

The action of bromine on the tetraethylacetal might prove of great interest, as the formation of addition-products from it similar to those obtained by J. U. Nef[1] from quinone, would prove that the four ethoxy groups were attached to the carbonyl radicles of the quinone molecule, and thus settle the constitution of this whole class of compounds. The chances

[1] This Journal, 12, 483.

of the formation of such addition-compounds were, however, small, as Nef has shown[2] that dichlordiethoxyquinone does not take up bromine, a result which we can confirm; nevertheless we felt that it would be unwise to neglect this experiment. Accordingly one-half gram of bromine dissolved in chloroform was added to one-half gram of the acetal also dissolved in dry chloroform. Even the first drop of the bromine imparted a distinct yellowish-red color to the solution, showing that no bromine addition-compound had been formed. When all the bromine had been added, the solution was allowed to evaporate spontaneously, and although the residue was colored slightly, it was found that the weight had not increased, and after one recrystallization from ligroïn it gave the melting-point of the unaltered acetal, 101°–102°. In another experiment the chloroform-solution was evaporated to dryness on the water-bath, and the same results were obtained. Under no conditions that we have found could the acetal be induced to take up bromine. The negative outcome of these experiments cannot be used in deciding the constitution of the acetal, since its inability to take up bromine is more likely to be due to the presence of the two atoms of chlorine and two ethoxy groups attached to the benzol ring than to the occupation of the double bonds by the four additional ethoxy groups, since dichlordiethoxyquinone does not take up bromine, as has been already stated.

Dichlordiethoxyquinone Dibenzoyldiethylacetal,

$$C_6Cl_2(OC_2H_5)_2(OC_2H_5)_2(OCOC_6H_5)_2.$$

When the diethylhemiacetal itself or its sodium salt was treated with benzoyl chloride at 100° in a sealed tube, no benzoyl compound was formed, but the main products were dichlordiethoxyquinone and ethyl benzoate. A similar result was obtained when the sodium or silver salt of the hemiacetal was suspended in ether, and then treated with benzoyl chloride. When, however, the sodium salt was suspended in alcohol instead of ether and benzoyl chloride added, the dibenzoyl derivative was readily formed, and only a trace of dichlordiethoxyquinone was produced. The following method

[2] This Journal, 11, 20.

was found to be the best for the preparation of this substance: To 10 grams of the sodium salt of the dichlordiethoxyquinone diethylhemiacetal suspended in a small quantity of alcohol 7.6 grams of benzoyl chloride were added, which gave the proportion of two molecules of benzoyl chloride to one of the sodium salt. There was but little action in the cold, but when the mixture was warmed on the water-bath the reaction took place readily, with the separation of sodic chloride. After cooling, the solution was filtered, and the solid remaining on the filter washed thoroughly with alcohol and water, and then crystallized from hot alcohol until it showed the constant melting-point 170°. The analysis of the substance dried at 100° gave the following results:

I. 0.2428 gram substance gave on combustion 0.5276 gram CO_2 and 0.1230 gram H_2O.

II. 0.2173 gram substance gave 0.1112 gram AgCl (Carius).

	Calculated for $C_6Cl_2(OC_2H_5)_2(OC_2H_5OCOC_6H_5)_2$.	Found. I.	II.
Carbon	59.47	59.27	....
Hydrogen	5.31	5.63	....
Chlorine	12.57	....	12.65

The yield of the dichlordiethoxyquinone dibenzoyldiethylacetal from 10 grams of the salt is 7.5 grams, or about 66 per cent. of the theoretical yield.

Properties of Dichlordiethoxyquinone Dibenzoyldiethylacetal.— From alcohol it crystallizes in short thick prisms, or, when crystallized more rapidly, in rhombic crystals with a sharp terminal angle, often collected into curving radiated or bladed groups. It is white, and melts at 170°. It is easily soluble in chloroform, carbonic disulphide, ether, or benzol; also in hot ethyl or methyl alcohol, but only slightly soluble in either of these liquids when cold; soluble in warm glacial acetic acid; slightly soluble in hot ligroïn; insoluble in water. Sulphuric acid of specific gravity 1.44 saponifies it, forming the compound described in the next section. Sodic hydrate solution, even if boiling or mixed with alcohol, does not decompose it.

The study of the action of reducing agents and of hydroxyl-

amine on the dichlordiethoxyquinone dibenzoyldiethylacetal was of special interest, because it threw so much light upon the constitution of this whole class of substances. If this body were a true acetal, these agents should have no action upon it; if, on the other hand, the ethoxy and benzoyl radicles were not attached to the two carbonyl groups of the quinone molecule, but to the four other atoms of carbon, the substance would be converted into a secondary alcohol by reducing agents, and into an oxime by hydroxylamine.

The reducing agent selected was a mixture of zinc-dust and glacial acetic acid, as this had proved rather the most effective for the conversion of a quinone into a hydroquinone, and there was little or no danger that it would saponify the compound. Even after long continued action there were no signs of reduction, but the unaltered dichlordiethoxyquinone dibenzoyldiethylacetal was recovered from the mixture. This experiment, therefore, goes to prove that the substance is an acetal, and this proof is strengthened by the fact that dichlordiethoxyquinone is converted into the corresponding hydroquinone quickly and easily by this reducing mixture.

To try the action of hydroxylamine 0.2 gram of the dichlordiethoxyquinone dibenzoyldiethylacetal dissolved in alcohol was mixed with an alcoholic solution of one-half gram of hydroxylamine chloride. The solution was boiled over the free flame for half an hour, and then after cooling treated with a large excess of water. The precipitate thus formed after one crystallization from alcohol melted at 170°, and was therefore the unchanged original substance. No other organic substance could be found in the precipitate, or in the aqueous filtrate. The experiment was repeated with an alkaline solution, and again with an acid solution, but in no case could any change in the original acetal be detected. To prove that the indifference of the acetal to the hydroxylamine was not due to the effect of the ethoxy radicles and chlorine atoms attached to its benzol ring, we next studied the action of the chloride of hydroxylamine on dichlordiethoxyquinone. For this purpose one-half gram of it was treated with the chloride of hydroxylamine in alcoholic solution, and the mixture warmed for sixteen hours on the water-bath. Water

precipitated a black substance crystallized in scales, which was thoroughly washed with water to remove all the hydroxylamine salt. It dissolved easily in sodic hydrate, and from this solution acids threw down a reddish gelatinous precipitate. It gave a good test for nitrogen by the potassium method. There can be no doubt, therefore, that the chloride of hydroxylamine acts on dichlordiethoxyquinone and consequently the indifference of our acetal to this reagent is not due to the presence of the radicles attached to the benzol ring, but is caused by the occupation of the two carbonyl groups by the ethoxy and benzoyl radicles. As we had accomplished our purpose when we had proved that the chloride of hydroxylamine acts on dichlordiethoxyquinone, we have not tried to study the product more carefully.

Saponification of Dichlordiethoxyquinone Dibenzoyldiethylacetal.

This substance was boiled with sulphuric acid of specific gravity 1.44, for half an hour in a flask with a return-condenser; a certain amount of gas was given off, and the solid finally went into solution completely, but upon cooling, crystals were deposited, the amount of which was increased by diluting the acid with water. This crystalline precipitate was filtered out, washed repeatedly with water to remove a little chloranilic acid which had been formed in the process, and the residue recrystallized from alcohol until it showed the constant melting-point 142°, when it was dried for analysis. The analysis of this substance gave a great deal of trouble; by using a boat and a stream of oxygen according to the usual method, we were unable to secure complete combustion, and therefore were forced to mix the compound with cupric oxide, and carry on the combustion in an old-fashioned closed tube. This accounts for the fact that our percentages of hydrogen are somewhat high.

I. 0.2119 gram substance gave on combustion, 0.4558 gram CO_2 and 0.0845 gram H_2O.

II. 0.2062 gram gave 0.4452 gram CO_2 and 0.0869 gram H_2O.

III. 0.2020 gram gave 0.4344 gram CO_2 and 0.0830 gram H_2O.

IV. 0.2063 gram gave 0.4451 gram CO_2 and 0.0837 gram H_2O.

V. 0.1947 gram substance gave 0.1136 gram AgCl (Carius).

VI. 0.2212 gram gave 0.1290 gram AgCl.

	Calculated for $C_{24}H_{28}O_7Cl_2$.	Found. I.	II.	III.	IV.	V.	VI.
Carbon	58.65	58.66	58.88	58.64	58.84	....	....
Hydrogen	4.07	4.43	4.67	4.56	4.51	....	....
Chlorine	14.46	....	....	....	....	14.42	14.41

The formula calculated from these analytical results is so strange, that we were at first unwilling to accept it, and thought that perhaps we had the dibenzoate of dichlordiethoxyhydroquinone in our hands, the calculated percentages of hydrogen and chlorine for which agree fairly well with those found by us, whereas the calculated percentage of carbon is over two per cent. higher. This difference we thought might be due to an obstinate impurity, and accordingly we prepared this dibenzoate from dichlordiethoxyhydroquinone, and found that it was entirely different from the saponification-product, as it melts at 215° instead of 142°. The description of this substance is given later in the paper. The supposition that the substance might contain an obstinately adhering impurity was disposed of by frequent recrystallizations. The sample for Analysis I. was crystallized only three or four times, that for II. and III. ten times, that for IV. eight times. There was no difference in the melting-points of these three samples, and, as the results given above show, no essential difference in their percentage composition. We must, therefore, accept the formula derived from these analyses, and the most probable hypothesis is that the atom of oxygen spans the benzol ring between two atoms of carbon in the para position, but we are unable to determine at present whether this atom of oxygen proceeded from the saponification of the ethoxy radicles of the acetal, and therefore lies between the two atoms of carbon to which the benzoate groups are attached, or from the two ethoxy groups of the chloranilic ester, and therefore spans the ring between two other atoms of carbon. This latter supposition seems to us the more probable, as it would give some explanation of the ease with which the ethyls are removed. We wished to confirm such an unusual hypothesis by studying the derivatives of this substance, but our work in this direction has not yet brought any conclusive evidence in regard to its constitution, and we therefore propose this theory only as the most probable one, leaving to future work the testing of its

accuracy. It may be observed here, that such a substance would be a natural product of the saponification of dichlordiethoxyquinone dibenzoyldiethylacetal as shown by the following reactions:

$$C_6Cl_2(OC_2H_5)_2(OC_2H_5)_2(OCOC_6H_5)_2 + 2H_2SO_4 =$$
$$C_6Cl_2(OC_2H_5)_2(OH)_2(OCOC_6H_5)_2 + 2C_2H_5HSO_4 =$$
$$C_6Cl_2(OC_2H_5)_2O(OCOC_6H_5)_2 + H_2O + 2C_2H_5HSO_4.$$

We would call the substance, in accordance with its provisional formula, oxide of dichlordiethoxyquinone dibenzoate, although it may be instead the oxide of dichlorquinone ethylbenzoylacetal.

Properties of the Oxide of Dichlordiethoxyhydroquinone Dibenzoate.—It crystallizes in white well developed six-sided prisms, often of considerable size, belonging either to the hexagonal or to the orthorhombic system. When crystallized more quickly, it forms rather loose rosettes of prisms terminated by several planes forming a very blunt end. It shows a strong tendency to separate from its solutions in the form of a varnish, this result being obtained, for instance, when the alcoholic solution is evaporated to dryness on the water-bath. It melts at 142°, and is readily soluble in alcohol or chloroform; soluble in carbonic disulphide, glacial acetic acid, or benzol; difficultly soluble in ether; insoluble in water. The best solvent for it is alcohol. With aniline it gives two or more products, the study of which next year, we hope, may throw some light on its constitution.

Reduction of the Oxide of Dichlordiethoxyhydroquinone Dibenzoate.

When the substance described in the preceeding paragraph is moistened with a concentrated solution of hydriodic acid, and heated on the water-bath until dry, a reaction takes place, as shown by the separation of free iodine. In order to complete the action the moistening with hydriodic acid and warming was repeated, and the product thus obtained was purified by repeated recrystallization from a very small quantity of alcohol until it showed the constant melting-point 164°, when it was dried at 100°, and analyzed with the following results:

I. 0.2004 gram substance gave on combustion 0.4339 gram CO_2 and 0.0812 gram H_2O.

II. 0.2301 gram substance gave 0.5001 gram CO_2 and 0.0825 gram H_2O.

III. 0.2274 gram substance gave 0.1462 gram AgCl (Carius).

IV. 0.1998 gram gave 0.1276 gram AgCl.

V. 0.1990 gram gave 0.1276 gram AgCl.

	Calculated for $C_6Cl_2(OC_2H_5)OH(OCOC_6H_5)_2$.	Found. I.	II.	III.	IV.	V.
Carbon	59.06	59.06	59.28	....	....	....
Hydrogen	3.58	4.50	3.99	....	....	....
Chlorine	15.89	....	....	15.90	15.79	15.85

These results agree best with those calculated for the formula given above, although it is not impossible that the substance may contain more hydrogen. It is obvious, however, that the formula of the substance cannot be considered as established, until the analytical data have been supported by experiments with some of its derivatives. We shall not at present indulge in any speculations on the constitution of this substance. It crystallizes usually in balls of indistinct little prisms, but occasionally slender short prisms terminated by a single plane at a very sharp angle were observed. Like its mother-substance, it has a strong tendency to come down from its solutions in the form of a varnish. It melts at 164°, and is very soluble in alcohol, much more so than the oxide from which it was obtained; easily soluble in acetone, or glacial acetic acid; sparingly soluble in ether, benzol, or chloroform; insoluble in carbonic disulphide, or water. It shows weak acid properties, since it dissolves in a solution of sodic hydrate, and is reprecipitated by an acid. Aniline acts upon it, but we have not yet studied the products. Alcohol seems to be the best solvent for it. The study of this substance will be continued in this laboratory next year, and we hope the results of this work will not only definitely establish its formula, but also throw much light on the constitution of the body we have called the oxide of dichlordiethoxyhydroquinone dibenzoate, from which it was obtained.

Dibenzoate of Dichlordiethoxyhydroquinone,

$C_6Cl_2(OC_2H_5)_2(OCOC_6H_5)_2$.

This substance, which was made in order to compare it with the oxide of dichlordiethoxyhydroquinone dibenzoate just described, was prepared as follows: The sodium salt of the substituted hydroquinone was treated with a slight excess of benzoyl chloride, and the product boiled with water to decompose the benzoyl chloride which had not entered into the reaction. After filtering hot the residue was recystallized from a mixture of alcohol and chloroform until it showed the constant melting-point 215°, when it was dried at 100°, and analyzed with the following result:

0.2000 gram substance gave 0.1202 gram AgCl (Carius).

	Calculated for $C_6Cl_2(OC_2H_5)_2(OCOC_6H_5)_2$.	Found.
Chlorine	14.95	14.86

Properties of the Dibenzoate of Dichlordiethoxyhydroquinone.—It crystallizes from a mixture of alcohol and chloroform in long white prisms terminated by two planes meeting at an obtuse angle; these prisms show a tendency to unite longitudinally. It melts at 215°, and is easily soluble in chloroform; soluble in boiling benzol; sparingly soluble in alcohol even when hot, or in glacial acetic acid; insoluble in ether, carbonic disulphide, ligroïn, or water. The dilute acids do not act on it even when boiling, nor does strong hydrochloric acid or strong nitric acid produce any visible effect; strong sulphuric acid also does not act on it in the cold, but when hot dissolves it, forming a slightly dark-colored solution. Alkalies even in strong boiling solution do not decompose it.

Dichlordimethoxyquinone Dibenzoyldimethylacetal.

$C_6Cl_2(OCH_3)_2(OCH_3)_2(OCOC_6H_5)_2$.

This substance was made in the hope that its saponification might throw some additional light on the curious products obtained from the corresponding ethyl compound, and described in the preceding sections. For this purpose 17 grams of the sodium salt of dichlordimethoxyquinone dimethylhemiacetal were suspended in methyl alcohol, and 20 grams of benzoyl chloride added (this is a little more than the calculated amount), after warming for a short time to finish the reaction, the liquid was allowed to cool, the solid, which had

separated, filtered out, and washed first with alcohol and afterward with water. The residue was purified by crystallization from a mixture of alcohol and chloroform until it showed the constant melting-point 193°, when it was dried at 100°, and analyzed with the following result:

0.2052 gram substance gave 0.1163 gram AgCl (Carius).

	Calculated for $C_6Cl_2(OCH_3)_2(OCH_3)_2(OCOC_6H_5)_2$.	Found.
Chlorine	13.95	14.02

The substance crystallizes from a mixture of alcohol and chloroform in several different forms, which, however, may be produced by the twinning of a single form in different ways. The simplest form observed consisted of rather long plates terminated by two planes at an obtuse angle to each other; these frequently appeared as broad plates in radiating groups, when less well developed. A second very common form was white thick plates, square or nearly so, which showed evidence of twinning, and finally mixed with these were sharp thick rhombic crystals looking like very acute scalenohedra, and showing a line of twinning along the diagonal between the two acute angles. Whether these were different habits of the same form, or indicated that the substance was not homogeous mattered little to us, as the saponification with sulphuric acid of specific gravity 1.44 gave a product which was evidently homogeneous, and this was the substance in which we were especially interested. The dichlordimethoxyquinone dibenzoyldimethylacetal is white, and melts at 193°. It is easily soluble in chloroform; soluble in benzol; sparingly soluble in alcohol, ether, glacial acetic acid, or carbonic disulphide; insoluble in water or ligroïn. The best solvent for it is a mixture of alcohol and chloroform.

Saponification of Dichlordimethoxyquinone Dibenzoyldimethylacetal.

The substance was boiled with sulphuric acid of specific gravity 1.44, in the manner already described under the corresponding ethyl compound, and the phenomena observed in this case were exactly similar to those presented by the ethyl compound. The product of the reaction was purified by recrystallization from a mixture of chloroform and alcohol until

it showed the constant melting-point 205°–206°, when it was dried at 100°, and analyzed with the following result:

0.2071 gram substance gave 0.1288 gram AgCl (Carius).

	Calculated for $C_6Cl_2(OCH_3)_2(OCOC_6H_5)_2O$.	Found.
Chlorine	15.33	15.38

This product therefore corresponds to that obtained by the saponification of the ethyl compound, and this view of its nature is confirmed by the striking similarity between these two substances in crystalline form.

Properties of the Oxide of Dichlordimethoxyhydroquinone Dibenzoate.—It crystallizes from a mixture of alcohol and chloroform in white well formed rhombic prisms, shorter than they are broad, terminated by a very obtuse octahedron and a basal plane forming a very blunt end; the prisms are frequently rendered six-sided by the presence of two basal planes on the acute edges. It melts at 205°–206°, and is readily soluble in chloroform; soluble in glacial acetic acid, or benzol; slightly soluble in alcohol, acetone, or carbonic disulphide; very sparingly soluble in ether; insoluble in water. The best solvent for it is a mixture of alcohol and chloroform.

Dichlordiethoxyquinone Diethylacetaldicarbonic Ester, $C_6Cl_2(OC_2H_5)_2(OC_2H_5)_2(OCOOC_2H_5)_2$.

After we had succeeded in replacing the sodium in the salts of the hemiacetals described in this paper with the benzoyl radicle, it seemed of interest to see whether other acid chlorides would act in the some way, and we therefore tried the action of chlorocarbonic ester. Four grams of the sodium salt of dichlordiethoxyquinone diethylhemiacetal suspended in absolute alcohol were mixed with a slight excess of chlorocarbonic ester, and warmed on the steam-bath for a few minutes in order to complete the reaction. The solution was filtered while still hot from the precipitate of sodic chloride, and the filtrate on cooling deposited well formed crystals of the new substance, which was purified by recrystallization from alcohol until it showed the constant melting-point 122°–123°, when it was dried, and analyzed with the following result:

0.1866 gram substance gave 0.1075 gram AgCl (Carius).

	Calculated for $C_6Cl_2(OC_2H_5)_2(OC_2H_5)_2(OCOOC_2H_5)_2$.	Found.
Chlorine	14.18	14.24

The substance crystallizes in white flat prisms, terminated usually by a single plane at a very sharp angle, which is occasionally modified by a second smaller plane. It melts at 122°–123°, and is readily soluble in alcohol, chloroform, benzol, or acetone; soluble in glacial acetic acid or carbonic disulphide; slightly soluble in ether; insoluble in water. The best solvent for it is alcohol. In view of the results of the saponification of the corresponding benzoyl compound the decomposition of this substance with sulphuric acid of specific gravity 1.44 promises to be interesting. Unfortunately, it was prepared just before the vacation, so that this work must be postponed until the next college year.

Action of Potassic Phenylate on Dichlordiphenoxyquinone—Tetraphenoxyquinone, $C_6(OC_6H_5)_4O_2$.

By treating 10 grams of pure dichlordiphenoxyquinone with a little more than two equivalents of potassic phenylate, made by dissolving 4 grams of potassic hydrate and 12 grams of phenol in 150 cc. of water, tetraphenoxyquinone was formed. In order to complete the reaction it was necessary to boil the dichlordiphenoxyquinone with the potassic phenylate for twenty to thirty minutes. The product formed was then filtered off, and after washing thoroughly with water and alcohol was purified by crystallization from benzol until it gave the constant melting-point of 229°–230°. After drying at 100°, the substance gave the following results on analysis:

I. 0.2198 gram substance gave on combustion 0.6122 gram CO_2 and 0.0865 gram H_2O.

	Calculated for $C_6(OC_6H_5)_4O_2$.	Found.
Carbon	75.63	75.97
Hydrogen	4.20	4.37

This body can also be formed by the action of four equivalents of potassic phenylate in aqueous solution on chloranil, or by the action of sodic phenylate on the dichlordiphenoxyquinone suspended in benzol. In this latter case the sodic phenylate was prepared by dissolving phenol in a rather large

volume of benzol, and then adding the required quantity of sodium, which disappeared completely after warming the solution on the steam-bath for some time. Neither of these methods gives so good a result as the one described at the beginning of this section. On the other hand, the tetraphenoxyquinone is not formed when the dichlordiphenoxyquinone is treated with sodic phenylate, which has been made by the action of metallic sodium on absolute alcohol mixed with phenol, as in this case the principal product is diethoxydiphenoxyquinone.

Properties of Tetraphenoxyquinone.—It crystallizes from benzol in red prisms which, when well developed, have blunt ends formed by a number of planes or by a single plane at an oblique angle. When smaller they appear as long somewhat shuttle-shaped prisms, radiating from a common centre, but not forming circular groups. It melts at 229°–230°, and is soluble in hot chloroform, boiling acetic anhydride, or boiling benzol; slightly soluble in carbonic disulphide, or boiling glacial acetic acid; very sparingly in warm acetone; insoluble in water, alcohol, ether, or ligroïn. The best solvent for it is boiling benzol.

The tetraphenoxyquinone is not easily attacked by reducing agents: sulphurous acid at ordinary temperatures, or in a sealed tube at 100°, has no action on it; hydriodic acid, or a mixture of stannous chloride and hydrochloric acid, reduces it, but the action is very slow; on the other hand, it is easily reduced by glacial acetic acid and zinc-dust.

Saponification of Tetraphenoxyquinone.

Toward acid saponifying agents the tetraphenoxyquinone shows a remarkable stability. Sulphuric acid of specific gravity 1.44 has no effect whatever, even after long continued boiling, but hot strong sulphuric acid of specific gravity 1.83 dissolves it, giving a solution from which nothing is precipitated on adding water. This may be due to the formation of a sulphonic acid, but we have not as yet studied the reaction carefully.

A better result was obtained by boiling the tetraphenoxyquinone with a solution of sodic hydrate (one part in four)

for about two hours, as it was then completely dissolved, giving a dark purple color to the solution, which on cooling deposited small black crystals of a sodium salt. The alkaline solution, when poured into an excess of dilute acid, gave a reddish-yellow precipitate, which was filtered out, washed with water, and, after purification by recrystallization from alcohol, dried, and analyzed with the following result:

0.2224 gram substance gave on combustion 0.5436 gram CO_2 and 0.0794 gram H_2O.

	Calculated for $C_6(OC_6H_5)_2(OH)_2O_2$.	Found.
Carbon	66.68	66.65
Hydrogen	3.70	3.97

The substance was therefore formed from the tetraphenoxyquinone by replacing two of the phenyl radicles by hydrogen, and is the diphenoxyanilic acid.

Properties of Diphenoxyanilic Acid, $C_6(OC_6H_5)_2(OH)_2O_2$.—It forms glistening, rather thick plates, either square or in rectangular oblong forms, having a dark reddish-brown color like that of ferric citrate, which the substance also resembles in lustre and general appearance. It melts at about 276°, but the melting-point is not sharp, as it shows signs of softening even at 270°. If heated somewhat above its melting-point, it puffs up, filling the capillary tube with a dark liquid. It is soluble in glacial acetic acid; sparingly soluble in alcohol or hot chloroform; insoluble in ether, benzol, carbonic disulphide, or ligroïn. It dissolves slightly in boiling water, imparting a pink color to the solution. It has distinct acid properties, dissolving in sodic hydrate to form a black crystalline salt, which dissolves in water with a dark purple color. It is not acted on by acids dilute or strong, cold or hot.

Tetraphenoxyhydroquinone, $C_6(OC_6H_5)_4(OH)_2$.

This body was made by reducing the tetraphenoxyquinone with glacial acetic acid and zinc-dust. Two grams of the tetraphenoxyquinone were warmed on the steam-bath with these reagents until the red color of the original substance had completely disappeared; water was then added, and the precipitated hydroquinone purified by recrystallizing it from alcohol containing a little hydriodic acid to prevent oxidation. On analysis the following results were obtained:

0.2015 gram substance gave on combustion 0.5558 gram CO_2 and 0.0862 gram H_2O.

	Calculated for $C_6(OC_6H_5)_4(OH)_2$.	Found.
Carbon	75.32	75.21
Hydrogen	4.60	4.75

Properties of the Tetraphenoxyhydroquinone.—It crystallizes from alcohol in white, well developed, rather thick rhombic plates, with a very acute angle, which sometimes show sharp notches in the two ends. When seen on the edge the plates seem to be monoclinic, and are often twined on the basal plane. Larger crystals are apt to have the form of sharp spear-heads. At 210° it shows signs of decomposition by beginning to turn red. This change of color increases as the temperature rises, until finally it melts at 219°–220°, giving a light red liquid, which on cooling solidifies to a red body, probably the quinone. It is readily soluble in acetone; somewhat more sparingly soluble in ethyl alcohol, methyl alcohol, or chloroform; sparingly soluble in cold glacial acetic acid, more readily in hot; very sparingly soluble in benzol or ether. It is insoluble in water, carbonic disulphide, or ligroïn. Alcohol is the best solvent for it.

Diethoxydiphenoxyquinone, $C_6(OC_2H_5)_2(OC_6H_5)_2O_2$.

This substance was obtained in some of our earlier attempts to make tetraphenoxyquinone by treating dichlordiphenoxyquinone with sodic phenylate dissolved in absolute alcohol. 10 grams of dichlordiphenoxyquinone were mixed with two equivalents of sodic phenylate made by treating 1.6 grams of sodium with about 20 cc. of absolute alcohol and then adding 8 grams of phenol. On the addition of the sodic phenylate the dichlordiphenoxyquinone became dark-colored, and a very black, tarry solution was obtained, which, after standing for two hours, was separated by filtration from the sodic chloride formed; water was then added to the filtrate, which precipitated an oily black liquid. In order to purify this liquid it was repeatedly washed with water by decantation, and then dissolved in alcohol, from which beautiful silky orange-yellow needles were obtained, and these were recrystallized from alcohol until they showed the constant melting-

point 128°, when after drying in a desiccator they gave the following results on analysis:

0.2104 gram substance gave on combustion 0.5324 gram CO_2 and 0.1004 gram H_2O.

	Calculated for $C_6(OC_2H_5)_2(OC_6H_5)_2O_2$.	Found.
Carbon	69.47	69.01
Hydrogen	5.26	5.30

The yield is small. The diethoxydiphenoxyquinone crystallizes in long silky orange-yellow slender needles arranged in radiating groups. It melts at 128°, and is readily soluble in alcohol or chloroform; soluble in carbonic disulphide or benzol; sparingly soluble in ether or glacial acetic acid; insoluble in ligroïn or water. The best solvent for it is alcohol.

Action of Sodic Methylate on Tetraphenoxyquinone—Dimethoxydiphenoxyquinone, $C_6(OCH_3)_2(OC_6H_5)_2O_2$.

When 5 grams of tetraphenoxyquinone were treated with a solution of 6 equivalents of sodic methylate in methyl alcohol, they dissolve to a colorless liquid, which on standing deposited a quantity of nearly white needles. These were filtered off, and, after washing with a little methyl alcohol, treated with water rendered alkaline by sodic hydrate, when a portion of the substance was dissolved, and a yellow crystalline body was left as an insoluble residue. This latter substance was purified by crystallization from a mixture of benzol and alcohol until it showed the constant melting-point of 171°, when it was dried at 100°, and analyzed with the following result:

0.2043 gram substance gave on combustion 0.5068 gram CO_2 and 0.0862 gram H_2O.

	Calculated for $C_6(OCH_3)_2(OC_6H_5)_2O_2$.	Found.
Carbon	68.19	67.66
Hydrogen	4.55	4.69

The substance is therefore dimethoxydiphenoxyquinone formed by the replacement of two of the phenyl by methyl radicles.

Properties of Dimethoxydiphenoxyquinone.—It crystallizes from a mixture of alcohol and benzol in beautiful long golden-yellow needles, which under the microscope are seen to be

slender prisms arranged in radiating groups. The terminations of these prisms consist of one principal plane, sometimes at a right angle, sometimes at an oblique angle to the sides; in this latter case, when the crystals are large enough, small modifying planes are also seen. It melts at 171°, and is readily soluble in chloroform; soluble in ethyl or methyl alcohol, benzol, or glacial acetic acid; sparingly soluble in ether or carbonic disulphide: insoluble in ligroin or water. It is reduced by zinc and glacial acetic acid to a colorless hydroquinone.

It dissolves apparently with decomposition in a dilute solution of sodic hydrate, and from this solution dilute sulphuric acid precipitates a non-crystalline body insoluble in water, but soluble in sodic hydrate with a fine purple color. We have not had time as yet to study this substance more carefully.

When the yellow dimethoxydiphenoxyquinone was mixed with a solution of sodic methylate in methyl alcohol, and the mixture stirred vigorously, the yellow solid disappeared, and a white crystalline sodium salt was precipitated. This precipitate dissolved in water without residue, and from the solution the addition of a dilute acid threw down a white amorphous solid, which decomposed almost immediately into a yellow substance, probably dimethoxydiphenoxyquinone. These observations show that in this case a hemiacetal was formed, but a much less stable one than that obtained from the quinones containing chlorine. It seems, therefore, that the stability of the hemiacetals depends on the number and strength of the negative radicles attached to the quinone ring.

Action of Sodic Phenylate on Bromanil.

In order to study this action 2 grams of bromanil, prepared according to Stenhouse,[1] were treated with an alcoholic solution[2] of sodic phenylate made by acting on 0.3 gram of sodium with absolute alcohol and then adding 3 grams of phenol. The bromanil began to turn red as soon as the phenylate was added, but it was necessary to warm the mixture in order to

[1] Ann. Chem. (Liebig) Suppl. 8, 13.

[2] This experiment was tried early in our work, before we had found that an aqueous solution of the sodic phenylate acted better on chloranil than the same reagent dissolved in alcohol. If we were to repeat this preparation, therefore, we should use a solution in water instead of in alcohol.

make the reaction complete. After this the solution was filtered, and the solid remaining on the filter, after thorough washing with water and alcohol, was purified by crystallization from benzol until it showed the constant melting-point 266°–267°, when it was dried at 100° and analyzed with the following result:

0.1677 gram substance gave 0.1393 gram AgBr (Carius).

	Calculated for $C_6Br_2(OC_6H_5)_2O_2$.	Found.
Bromine	35.56	35.36

The substance is, therefore, dibromdiphenoxyquinone, and it is to be observed that bromanil behaves differently from chloranil with this alcoholic solution of sodic phenylate, for the latter lost all four of its atoms of chlorine, two being replaced by phenoxy and two by ethoxy groups. The bromanil, on the other hand, behaves with the alcoholic solution of sodic phenylate as chloranil does with an aqueous solution of this reagent, the action consisting in the replacement of two atoms of halogen by two phenoxy groups.

Properties of Dibromdiphenoxyquinone.—It crystallizes from benzol in rather short orange-red needles with blunt points, melting at 266°–267°. It is very slightly soluble in alcohol even when hot; insoluble in ether or ligroïn, or in water whether cold or hot; sparingly soluble in carbonic disulphide or boiling benzol, and only very slightly soluble in cold benzol; more soluble in chloroform; freely soluble in hot glacial acetic acid, slightly in cold. The three strong acids have no visible effect upon it. By the action of glacial acetic acid and zinc-dust it is reduced to a colorless hydroquinone. It reacts easily with sodic methylate, ethylate, or phenylate, and also with sodium malonic ester, or aniline, but we have studied only its action with sodic methylate.

Dibromdimethoxyquinone Dimethylhemiacetal,
$C_6Br_2(OCH_3)_2(OH)_2(OCH_3)_2$.

This body was formed by treating 1.4 grams of dibromdiphenoxyquinone with a solution of rather less than four equivalents of sodic methylate in methyl alcohol, which was made by the action of a little methyl alcohol on 0.3 gram of metallic sodium. When the sodic methylate was first added,

there was no apparent action, but after warming on the steam-bath for a few minutes a white crystalline sodium salt separated. The salt was filtered out, washed with a little methyl alcohol, dissolved in water, filtered again, and then dilute sulphuric acid added in excess, which gave a bulky white precipitate. This was filtered off, washed with water, alcohol, and ether, and then dried for a short time over sulphuric acid and paraffine. The product was analyzed with the following results:

0.2047 gram substance gave 0.1966 gram AgBr (Carius).

	Calculated for $C_4Br_2(OCH_3)_2(OH)_2(OCH_3)_2$.	Found.
Bromine	41.03	40.88

The dibromdimethoxyquinone dimethylhemiacetal is a white amorphous solid insoluble in all the common solvents. It melts at 178°–188°, at the same time changing to a red substance, probably dibromdimethoxyquinone. The change can also be produced by treatment with dilute sulphuric acid, or dilute hydrochloric acid. From this description of the preparation and properties of this hemiacetal it is evident that the action of sodic methylate on dibromdiphenoxyquinone is similar in every respect to the action of this reagent on the corresponding compound containing chlorine.

Action of Potassic Phenylate on Trichlorquinone.

By treating 5 grams of trichlorquinone suspended in water with 2 equivalents of potassic phenylate, made from 2.7 grams of potassic hydrate and 8 grams of phenol, a semi-liquid substance was formed. After the mixture had been heated on the steam-bath for twenty minutes in order to complete the reaction, the supernatant liquid was poured off, and the pasty residue washed with water by decantation, and then warmed with alcohol, which converted it into a crystalline solid. These crystals were then separated by filtration, washed thoroughly with cold alcohol, and recrystallized from alcohol containing a small amount of benzol until they showed the constant melting-point 169°–170°, when they were dried at 100°, and analyzed with the following results:

I. 0.1888 gram substance gave 0.0818 gram AgCl (Carius).

II. 0.1913 gram substance gave 0.0832 gram AgCl.

	Calculated for $C_6HCl(OC_6H_4)_2O_2$.	Found. I.	II.
Chlorine	10.87	10.71	10.75

Properties of Monochlordiphenoxyquinone.—It crystallizes from alcohol in long, slender, pointed oval plates arranged in irregular groups,—a very characteristic habit of crystallization. It has an orange color, with a slight brownish tinge, and melts at 169°–170°. It is easily soluble in benzol or chloroform; difficultly soluble in alcohol; slightly soluble in carbonic disulphide; insoluble in water, ether, or ligroïn. It is easily reduced to a colorless hydroquinone by glacial acetic acid and zinc-dust.

To see whether it would form a hemiacetal, 0.5 gram of the monochlordiphenoxyquinone was treated with the sodic methylate made by acting on 0.3 gram of metallic sodium with a few cc. of methyl alcohol. The quinone dissolved in the cold, but, even when allowed to stand for some time and stirred vigorously, no precipitate of a sodium salt was formed. When, however, it was warmed for a few minutes, a heavy white precipitate was deposited, which, after being washed with a little methyl alcohol, dissolved completely in water, giving a clear solution. The addition of an acid to this solution produced a turbidity, which soon developed into a white precipitate, undoubtedly the hemiacetal, but this passes so easily into a red quinone-derivative that we have not attempted to analyze it, especially as its properties leave no doubt as to its nature. It follows from these observations that the stability of the hemiacetals is increased by the number of negative radicles, such as chlorine atoms, present.

Action of Sodic Ethylate on Quinone.

Although the results described in the last section made it probable that the hemiacetal derived from quinone itself would be very unstable, we have tried some experiments on the action of sodic ethylate on quinone ($C_6H_4O_2$), and think it best to give a preliminary account of them here, in spite of the fact that they have not led as yet to any definite result. They have, however, proved that sodic ethylate acts on quinone, but have by no means convinced us that the product is a hemiacetal. On treating quinone dissolved in ether with

an alcoholic solution of sodic ethylate, a heavy, flocculent, dark-green precipitate is formed, which is insoluble in ether, but dissolves in alcohol or water with decomposition. This precipitate does not seem to be homogeneous, as by fractional precipitation products were obtained unlike in color, and also in their composition, as shown by analysis; moreover its study is rendered difficult by the fact that it takes fire spontaneously when dried at ordinary temperatures in the air; if, however, it is dried in an atmosphere of hydrogen, it can be exposed to the air without taking fire at ordinary temperatures, but, if warmed to 40°, it begins to glow, and burns like tinder. Before studying this rather unmanageable substance further, we tried to get some idea of the way in which the reaction ran by a quantitative study of it, based upon the fact that all the quinone can be removed from its ethereal solution by the sodic ethylate.

In the first trial it was found that 1 gram of quinone required 0.2352 gram of sodium for complete precipitation.

In the second trial 1 gram of quinone required 0.2460 gram of sodium.

In the third trial, 3 grams of quinone required 0.6 gram of sodium.

These results indicate that each molecule of quinone acts with only 1 molecule of sodic ethylate, as the amount of sodium needed in this case for 1 gram of quinone is 0.213 gram, and the observed results come as near to this number as could be expected, when the roughness of the method is considered. This conclusion is confirmed by the yield of the salt obtained from 3 grams of quinone, which was 4.7 grams, whereas, if only 1 molecule of sodic ethylate had been added to each molecule of the quinone, the yield should have been 4.9 grams. The study of other parts of this research has occupied our time so completely that we have been unable to do more on this division of the subject, but we hope that this work can be taken up again in this laboratory at an early date.

Experiments on Phenoquinone.

It has been suggested in the introduction that phenoqiu-

none and quinhydrone may be hemiacetals similar to those studied in this paper. In that case phenoquinone should contain two hydroxyl groups, and form salts. Accordingly, we have tried to obtain a salt of it, although the chances of success were not great, as Wichelhaus[1] has stated that phenoquinone forms no salts, but is decomposed by alkalies. Still we thought that possibly by using sodic ethylate in insufficient quantity we might succeed, as the replacement of the hydrogen by the metal might take place in preference to the decomposition of the phenoquinone, especially as Wichelhaus also states that it gives a blue color with alkalies. We proceeded as follows: One gram of phenoquinone[2] was dissolved in ether, and treated with an alcoholic solution of the sodic ethylate made from 0.1 gram of sodium; as 0.154 gram of sodium would be required for two atoms of sodium to each molecule of phenoquinone, there was a considerable excess of this latter substance. As soon as the sodic ethylate was added, a heavy, flocculent, dark-green precipitate was formed, which was filtered out, washed thoroughly with ether, and dried over sulphuric acid and paraffine. We hoped at first that this was the salt of phenoquinone, and three sodium determinations seemed to confirm this idea, as they gave 13.14, 13.41, and 14.31 per cent. of sodium, which is not far from the number calculated for a sodium salt of phenoquinone, since that is 13.52 per cent. of sodium; but the study of the ethereal filtrate from the salt threw a great deal of doubt on this conclusion, since it contained a large amount of phenol. We think it more probable, therefore, that the sodic ethylate decomposed the phenoquinone into quinone and phenol, and that the green salt was then formed by the action of the sodic ethylate upon the quinone, the action being the same as that described in the last section. This inference is strengthened by the marked resemblance in appearance between the salts obtained in these two cases, and also by the study of the

[1] Ber. d. chem. Ges., **5**, 248.

[2] The phenoquinone was made by adding 1 equivalent of quinone dissolved in hot ligroïn to 2 equivalents of phenol dissolved in a small quantity of the same solvent. The mixed solutions were warmed for a few minutes, and then on cooling beautiful red crystals separated, which were purified by recrystallization from alcohol.

properties of the salt made from the phenoquinone, since it dissolved completely in water, forming a dirty-green solution, and undoubtedly suffering partial decomposition, as ether extracted from this solution colorless crystals of hydroquinone recognized by their melting-point of 169°. The addition of an acid to this solution gave no precipitate, and upon shaking out the acidified liquor with ether, nothing was extracted but hydroquinone. If the substance had been the desired salt of phenoquinone, phenol should have been obtained from this filtrate. Although these experiments tell against the formation of salts of phenoquinone, we do not consider them absolutely final, but the study of the action of alkalies on phenoquinone under other conditions will be continued in this laboratory during the coming college year.

As we had not succeeded in making a salt of phenoquinone we next turned our attention to the action of sodic phenylate on quinone, as, if the phenoquinone is a hemiacetal, this should act as well as free phenol, whereas, according to the other theories of the constitution of phenoquinone, it is hard to see how there should be any action in this case. Sodic phenylate was made by warming the proper amount of metallic sodium with a solution of phenol in benzol until the sodium had entirely disappeared. As the benzol cooled, the white crystalline sodic phenylate separated abundantly, and, after filtering, any free phenol was removed by washing with cold benzol. Upon adding the solid sodic phenylate to a solution of quinone in absolute ether a dark red crystalline substance looking like phenoquinone was formed. After evaporating off the ether slowly, the residue dissolved easily in water with a slight green color, and acids precipitated from this aqueous solution a small amount of a dark reddish solid. The ethereal solution showed a tendency to turn green round the edges during the evaporation which may perhaps have been due to the action of the moisture in the air. If benzol was used to dissolve the quinone instead of ether, a pink substance was formed, which changes to a dark-green body when warmed. With ligroïn as the solvent, a dark-green precipitate was obtained at first. Unfortunately, this work was undertaken at the very end of the term, so that a more careful study of these

products must be postponed until next year, but these preliminary experiments show that sodic phenylate does combine with quinone, and therefore lend a certain amount of countenance to our suggestion that phenoquinone is a hemiacetal.

Contributions from the Chemical Laboratory of Cornell University.

PARANTHRACENE OR DIANTHRACENE: A POLYMERIC MODIFICATION OF ANTHRACENE.

By W. R. Orndorff and F. K. Cameron.

The remarkable change which anthracene (or photene) undergoes when its solution in alcohol or benzene is subjected to the direct action of the sun's rays, was first observed in 1866 by J. Fritzsche,[1] who gave the name paraphotene to the product formed. A little later Graebe and Liebermann[2] also noticed this peculiar transformation of anthracene, but they called the compound which separates out of the solutions "paranthracene," as they had previously shown that Fritzsche's photene was identical with the anthracene of Laurent and Anderson. This substance was characterized by its insolubility in all the usual solvents, its indifference to both nitric acid and bromine and the fact that at its melting-point, 244°, it is changed into anthracene melting at 213°.

In 1874 E. Schmidt[3] investigated paranthracene with the idea of obtaining from it nitro derivatives of anthracene, as it resisted the action of reagents and appeared to be more stable than anthracene itself. He confirms the statement of the previous investigators in regard to its insolubility, its reversion into anthracene at its melting-point (244°–245°), and the fact that it is not acted upon by bromine or nitric acid. With picric acid it forms no compound as anthracene does, and when it is acted upon by the strongest reagents it gives, according to Schmidt, substitution-products of anthracene, being apparently first converted into that hydrocarbon.

No further work appears to have been done on paranthracene till 1891, when K. Elbs[4] attempted to determine the mole-

[1] J. prakt. Chem. **101**, 337; **106**, 274; Ztschr. Chem. 1867, 290.
[2] Ann. Chem. (Liebig) Suppl. **7**, 264 (1870).
[3] J. prakt. Chem. [2] **9**, 247.
[4] *Ibid.*, [2] **44**, 467.

cular weight of the substance by the freezing-point method. The product with which Elbs worked is described as melting not quite sharply at 272°–274°, and the statement is made that it remained unchanged when heated alone to 260° or when its solution in dimethylaniline was boiled, though it was partially converted into anthracene when heated in naphthalene to the boiling-point of that substance (218°) and completely when warmed to 260° in diphenylamine. Elbs found that paranthracene exhibited no fluorescence either in solution or in the solid form, and was extraordinarily insoluble in the usual solvents. In naphthalene, the material selected by Elbs for the molecular-weight determinations, it dissolves to the extent of only 0.229 parts in 100 of the solvent at the melting-point, so that the depressions of the freezing-point measured are necessarily very small. To eliminate experimental errors as much as possible, it was found necessary therefore to estimate the melting-point of the pure naphthalene as well as that of the solution, as the mean of a series of determinations. "In dieser Weise," he continues, "ergab sich aus 10 Reihen mit im Ganzen 118 Einzelablesungen als mittleres Moleculargewicht des Paranthracens die Zahl 303, wobei der niedrigste beobachtete Werth 248, der höchste 344 war; beistehend eine zusammengehörige Gruppe von Messungen, ausgeführt mit einem einfachen Beckmann'schen Apparat, dessen Thermometer in $\frac{1}{50}°$ eingetheilt ist:

Procentgehalt der Lösung.	Depression.	Molecular-gewicht.	Anzahl der Versuche.
0.059	0.012°	344	7
0.108	0.023	329	7
0.132	0.027	342	7
0.146	0.037	276	8
0.229	0.053	303	10 "

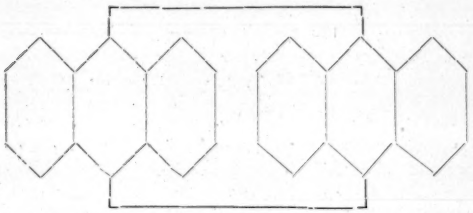
From these results Elbs concludes that paranthracene is formed from anthracene by the combination of two molecules of the latter. He found it impossible to make derivatives of paranthracene by the action of any reagent. The products he obtained were either indefinite or derivatives of anthracene itself. When treated with bromine in the sunlight both anthracene and paranthracene gave the same product, dibromanthracene tetrabromide.

In regard to the relation between anthracene and paranthracene he says nothing further.

The most recent work on paranthracene is that of Linebarger,[1] who made the substance by exposing anthracene to the sunlight in benzene, toluene, xylene, ethylbenzene, alcohol, acetic acid, ethyl benzoate, benzene bromide, chloroform, ethylene bromide, and carbon bisulphide. The melting-point of the material obtained from all the above liquids except ethylene bromide and carbon bisulphide varied from 243° to 245, the low melting-points of the material from ethylene bromide (210°–212°) and carbon bisulphide (207°–211°) being due, according to Linebarger, to the fact that these solvents are themselves decomposed by light and the substance was contaminated with the decomposition-products of the solvents. As to the way in which the two molecules of anthracene combine to form one molecule of paranthracene, Linebarger offers the following hypothesis, basing his conclusions on the work of Elbs: "It is pretty well established that in anthracene the so-called γ-carbon atoms have one bond in common, *i. e.*, anthracene may be regarded as ethane in which four of the hydrogen atoms are replaced by two bivalent radicles, *viz.*, phenylene; or what amounts to the same thing, anthracene consists of *three benzene rings*, of which the middle one has two of its carbon atoms, in the para position bound directly together. This double (?) linkage of the γ-carbon is quite loose, as shown by the ready oxidation of anthracene into anthraquinone, and the formation of addition-products with chlorine and bromine at low temperatures. It might be now, that by the action of the sun's rays these double (?) bonds would be set free in some way. If, then, a molecule of anthracene with its double (?) bonds thus loosened should come within the sphere of action of another molecule in a similar condition, the free bonds of the one molecule might unite with the free bonds of the other, doubling up and forming a new molecule, stable so far as the action of the light is concerned. In direct sunlight, the equilibrium of the anthracene molecule is *labile*, while that of the paranthracene is *stable*. On the other hand, under the influence of heat the

[1] This Journal, **14**, 597.

paranthracene is in labile, and the anthracene in stable equilibrium, for at 244° the double molecule decomposes into two simple ones—paranthracene changes into anthracene. There is then in paranthracene a *ring of four carbon atoms*, occupying with respect to the anthracene molecule the *γ*-position." In the *Jahrbuch der Chemie* for 1893 (p. 147), this idea of Linebarger's is given expression in the following formula :



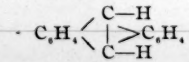
It will be seen from this review of the subject that the exact relation between anthracene and paranthracene is not yet determined. No analyses of paranthracene have been made, or at least if made they have not yet been published, so that it is by no means certain that anthracene and paranthracene have the same percentage composition. All previous investigators seem to have been satisfied that anthracene and paranthracene had the same percentage composition because anthracene changed into paranthracene in the sunlight, and on heating paranthracene to its melting-point (244°), it gave a product which, after solidification, melted at 213°, the melting-point of anthracene.

It will be seen too that the determinations of the molecular weight of paranthracene made by Elbs are far from satisfactory. Owing to the slight solubility of the material in naphthalene at its point of solidification the depressions measured by the thermometer graduated *in fiftieths of a degree* were only 0.012—0.053°. This fact makes a very small experimental error of great importance in the molecular-weight column. For example, a difference of 0.01° in the readings will frequently change the result from the double to the single molecule. In addition to this the fact that the paranthra-

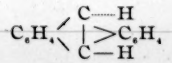
cene with which Elbs worked melted at 272°–274°, while all the other investigators give the melting-point as about 244°, would seem to indicate that his material was impure.

In his molecular-weight determinations it will be noted that in one case Elbs worked up to the limit of solubility of paranthracene in naphthalene which might vitiate these results on account of the possibility of some of the dissolved material separating out when the temperature of the solvent is lowered to determine the freezing-point. Besides this it is well-known that it is no easy matter to make molecular-weight determinations by the freezing-point method in such a high melting and volatile substance as naphthalene. Moreover, these results of Elbs have never been confirmed by any other chemist nor have like results been obtained with any other solvent than naphthalene, so that the molecular weight of paranthracene may be still regarded as doubtful.

Furthermore, from a comparison of the physical properties of anthracene and paranthracene, and the fact that each may be readily transformed into the other and that both give the same products when acted on by the same reagents, it will be seen that these two substances bear to each other much the same relation as that frequently observed between two stereoisomers. If now the space-formula for anthracene be examined it will be found that it admits of two configurations, the one corresponding to the *cis*, the other to the *trans* form, as shown in the following formulas, in which the dotted line represents the hydrogen atom below the plane of the paper, and the unbroken line that above:



Cis form.



Trans form.

It seemed highly desirable, therefore, that further and more careful work should be done before any speculations as to the structural formula of paranthracene and its relations to anthracene were indulged in. Pure paranthracene was therefore made, analyzed, and its properties and crystal form carefully studied. The molecular weight of the pure substance was then determined by the boiling-point method, which has

the great advantage over the freezing-point method, in that paranthracene is very much more soluble in liquids at their boiling-points than at their freezing-points, consequently the rise in the boiling-point is much greater than the depression of the freezing-point, so that errors of observation do not affect the final results to anything like the same degree. Regarding certain other advantages that the boiling-point method of determining molecular weights has over the freezing-point method the reader is referred to a recent communication by us.[1]

EXPERIMENTAL.

The paranthracene was made by exposing purified anthracene suspended in benzene and xylene in thin white glass bottles, to the direct action of the sunlight for some weeks during the Summer and Fall of the year 1894. The bottles were shaken from time to time to remove as soon as possible the materials from the sides and to dissolve the anthracene remaining unacted upon at the bottom of the bottles. By this means the action of the sunlight was not prevented by the opaque material adhering to the sides of the bottles and the conversion of the anthracene into paranthracene was completed in a much shorter time. When paranthracene no longer separated out the solid material was filtered from the liquids, which were generally colored reddish yellow, washed with benzene and dried. This crude material was boiled in a flask connected with a reflux condenser, first with alcohol, then with acetic ether and finally with benzene, in order to remove substances soluble in these liquids. The material left, which was pure white and crystalline, was dried and recrystallized at least three times from benzene. Dimethylaniline, recommended by Elbs as a solvent, was found unsuitable as it changes color when heated and the paranthracene was partially converted into anthracene at the boiling-point of this solvent. Xylene was found to be well adapted to the purpose, but benzene gave the best results. Owing to the very slight solubility of the paranthracene in benzene the following method was adopted for its recrystallization: A shell made of filter-paper and containing the material to be recrystallized was introduced into a fat-

[1] This Journal, **17**, 517.

extractor, in which the extraction takes place at the boiling-point of the solvent; the lower end of the extractor was then connected with a round-bottomed flask containing *pure* benzene and the upper part with an Allihn condenser. In this apparatus when the benzene is heated to the boiling-point the extraction and filtration take place automatically so that the use of large quantities as well as any loss of the solvent is avoided. This method was found to work remarkably well with slightly soluble materials and can be highly recommended.

The products of the different crystallizations were checked by combustion analyses[1] with the following results:

First recrystallization:

0.2746 gram gave 0.9018 gram CO_2 and 0.1412 gram H_2O.

	Found.	Calculated for $C_{14}H_{10}$.
Carbon	89.56	94.38
Hydrogen	5.71	5.62
	95.27	100.00

Second recrystallization:

0.3182 gram gave 1.0885 grams CO_2 and 0.1610 gram H_2O.

	Found.
Carbon	93.29
Hydrogen	5.61
	98.90

Third recrystallization:

I. 0.1478 gram gave 0.5076 gram CO_2 and 0.0760 gram H_2O.
II. 0.1576 gram gave 0.5424 gram CO_2 and 0.0796 gram H_2O.
III. 0.1828 gram gave 0.6304 gram CO_2 and 0.0923 gram H_2O.

	Found.		
	I.	II.	III.
Carbon	93.66	93.87	94.05
Hydrogen	5.71	5.64	5.64
	99.37	99.51	99.69

Fourth recrystallization:

I. 0.2094 gram gave 0.7229 gram CO_2 and 0.1103 gram H_2O.
II. 0.2369 gram gave 0.8201 gram CO_2 and 0.1226 gram H_2O.
III. 0.18825 gram gave 0.6517 gram CO_2 and 0.0983 gram H_2O.

[1]The first and second analyses were made by W. R. O., using lead chromate and lead oxide (method of de Roode: This JOURNAL, 12, 226); the others were made with copper oxide and oxygen in an open tube, by one of the students in the laboratory, Mr. D. A. Morton, to whom we wish here to express our thanks.

	Found. I.	II.	III.
Carbon	94.15	94.31	94.40
Hydrogen	5.89	5.75	5.80
	100.04	100.06	100.20

From these results we may conclude that pure paranthracene and anthracene have the same percentage composition. The paranthracene is probably accompanied by some other hydrocarbon[1] containing a relatively larger proportion of hydrogen and less carbon, from which it could only be completely separated by very many crystallizations. The pure product was a beautifully white crystalline substance melting at 242°–244° C. to a light yellow liquid which on cooling solidified to a white substance, showing, however, some green discoloration, but which melted sharply at 213° (standardized thermometer). The purest specimens of anthracene and paranthracene we could prepare showed more or less of this green color after melting, so that it seemed practically impossible completely to eliminate the substance to which it is due. The solid obtained from the melted paranthracene was identified as anthracene, possessing all the characteristics of that substance, and exhibiting a well marked violet fluorescence both in the solid form and in solution. The transformation of the paranthracene into anthracene appears to be quantitative and it may be brought about at a somewhat lower temperature (230°–235°) by prolonging the heating at this point. It takes place at a still lower temperature in boiling liquids in which it is soluble, for example in boiling naphthalene (218°) and partially in dimethylaniline (192°) and even to some extent in boiling aniline (182°).

Pure paranthracene shows no trace of the violet fluorescence so characteristic of anthracene, either in the solid form or in solution, nor does it combine with picric acid to give an addition-product analogous to the red compound anthracene forms. It differs most markedly from anthracene, however, in its solubility in various liquids. While anthracene dissolves quite readily in most of the ordinary organic solvents, paranthracene is insoluble or difficultly soluble in nearly all of

[1]See Thorpe's Dictionary of Applied Chemistry, Vol. 1, p. 175.

them. It is practically insoluble in methyl and ethyl alcohols, ether, carbon bisulphide, chloroform, glacial acetic acid, petroleum-benzine, acetone and acetic ether, though it is sparingly soluble in the hydrocarbons of the benzene series at their boiling-points, being more soluble the higher the boiling-point of the solvent. It is slightly soluble in boiling ethylene bromide (0.2273 gram in 100 of ethylene bromide), much more soluble in pyridine at its boiling-point (1.106 grams in 100 of pyridine), and still more soluble in boiling anisol (1.46 grams in 100 of anisol) and in phenetol (1.50 grams in 100 of phenetol).

The specific gravity of anthracene at 27° compared with water at 4° is 1.250, while that of paranthracene is 1.265 as shown by the following determinations made with the *purest* fine ground materials:

ANTHRACENE.

Gram substance.	Wt. equal vol. water.	Specific gravity at 27°.
0.3085	0.2532	1.258
0.2475	0.1674	1.253
	Average	1.256

$\frac{1.256}{1.003472^{1}} = 1.250$ specific gravity at 27° compared with water at 4°.

PARANTHRACENE.

Gram substance.	Wt. equal vol. water.	Specific gravity at 27°.
0.2612	0.2053	1.272
0.3495	0.2763	1.266
	Average	1.269

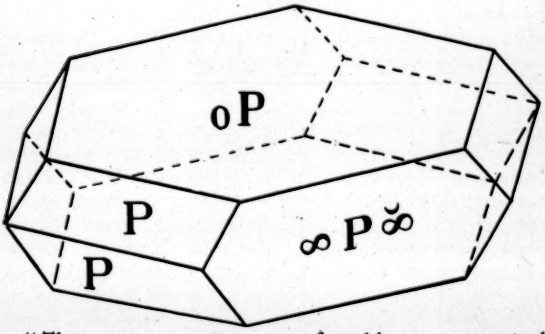
$\frac{1.269}{1.003472^{1}} = 1.265$ specific gravity at 27° compared with water at 4°.

Paranthracene differs from anthracene also in its crystal form and optical constants, as will be seen from the following report, for which we are indebted to Professor A. C. Gill of the Mineralogical Department of this University.

"Measurements of paranthracene crystals give results as follows:

[1] One cubic centimeter of water at 4° will give 1.003472 cc. at 27°—Ostwald: *Physico-Chemical Measurements.*

System Orthorhombic, $a:b:c = 0.6762:1:1.5731$
Faces observed, oP (001), P (111), and $\infty P\breve{\infty}$ (010)
Angles measured, $oP:\infty P\breve{\infty} = 90° 1'$
$oP:P = 70° 24'$
$\infty P\breve{\infty}:P = 58° 9'$



"These measurements were confirmed by measurement of the plane angles on the stage of a microscope:

"Calculated angle between intersections of pyramid faces with base = 111° 52′; average of 31 measurements 111° 55′; calculated angle of pyramid intersections on the brachypinacoid 133° 28′; average of 17 measurements 133° 24′.

"The habitus of the crystals is very variable. They are usually extremely thin tabular,—much thinner than shown in the figure. Frequently the development of pyramid faces is such as to give a monoclinic appearance, more rarely an orthorhombic hemimorphic shape; and in a few cases a stout columnar form was observed. The largest crystals (from anisol) attained a length of 6 mm., with a thickness of only 0.2-0.3 mm.

"All crystals show parallel extinction on both of the pinacoids. Double refraction strong in basal plates, 0.39 as determined by interference colors. Plane of optical axes = ∞P. The positive bisectrix is normal to the base, so crystals usually give an excellent interference figure in converged polarized light. Optical angle in water with sodium light, 81° 34′.

"The close relationship of this substance to anthracene has suggested a comparison of their crystal forms. The measurements of Kokscharow[1] on anthracene are used in the comparison. The ratio $a:b$ in anthracene is 1.422 : 1, that of $b:a$ in paranthracene is 1.479 : 1. If, then, paranthracene be considered as derived from anthracene by repeated (molecular?) twinning parallel to the tabular face, the following coincidences are to be observed: (1) The paranthracene crystals are orthorhombic. (2) The corresponding lateral axes in anthracene and paranthracene are 1.422 and 1.479, respectively. (3) The tabular faces (taken as the base for each substance) coincide. (4) The pyramid faces of paranthracene should be made up of a sub-microscopic oscillatory combination, as it were, of the faces $+P$ and ∞P of anthracene. Of these, it is conceivable that ∞P should have a greater effect on the position of the pyramid faces of paranthracene, since it is more largely developed on anthracene than is $+P$. It is found, in fact, that the angle between ∞P and oP of anthracene is 68° 30′, that between $+P$ and oP is 82° 22′, while in paranthracene the angle between P and oP is 70° 24′, an intermediate value, but more nearly approaching the 68° 30′ angle.

"The relationship between the forms of these two substances would seem to afford ground for suggestive speculations on their actual stereochemical crystal and molecular structure."

The conversion of anthracene into paranthracene takes place when solutions of anthracene are exposed to the sunlight, and also less rapidly in diffused daylight. The light of the electric arc will bring about the change though much more slowly. This peculiar transformation seems to be connected in some way with the absorption of light and the fluorescence of solutions of anthracene. The radiant energy is, perhaps, partially transformed in the solutions of anthracene into chemical energy, which converts the anthracene into paranthracene, the insolubility of the latter aiding in carrying the reaction to completion.

Many attempts were made to bring about the transformation of anthracene into paranthracene by other methods, but

[1]N. Petersb. Acad. Bull. 11, (1867), 385.

in no case were they successful. Some of the methods are here enumerated: paranthracene was dropped into melted anthracene at various temperatures from 215°–240° but it was entirely converted into anthracene, the entire material solidifying as such. Anthracene suspended in concentrated hydrochloric acid was heated in a sealed tube to 220° for about seven hours. The anthracene was converted into a greenish-white pulp but was found to dissolve completely in alcohol, no trace of paranthracene being obtained. Anthracene suspended in alcohol saturated with hydrochloric acid gas was heated in a sealed tube to 220° for eight hours. No paranthracene could be detected in the material resulting. Specimens of anthracene and paranthracene heated alone in sealed tubes gave identical results. A part of the material was carbonized, but a part sublimed as anthracene in wide six-sided plates, perfectly colorless and transparent but showing an intense violet fluorescence and displaying very beautiful and striking interference-figures in converged polarized light. Some very pure anthracene was suspended in alcohol and reduced with sodium amalgam according to the method of Graebe and Liebermann,[1] and then boiled for some time with an excess of the amalgam. The conversion of the anthracene into anthracene dihydride ($C_{14}H_{12}$) was complete but no paranthracene could be detected. Anthracene dibromide ($C_{14}H_{10}Br_2$), made by the method of Perkin,[2] was treated with zinc dust in carbon bisulphide at about 0°, the whole mass then allowed gradually to warm up to the temperature of the room, the carbon-bisulphide solution becoming colored, first green and then brown. After evaporating off the solvent in a current of air the residue was found to consist of anthracene, zinc bromide, and a gummy material entirely soluble in alcohol, no trace of paranthracene being found. A solution of pure anthracene in benzene was treated with sodium and boiled for some time in a flask connected with a reflux condenser. No paranthracene was found in this experiment, the anthracene remaining unchanged.

Having determined that paranthracene and anthracene

[1] Ann. Chem. (Liebig) Suppl., **2**, 265.

[2] Chem. News, **34**, 145; Bull. Soc. chim. (Paris), [2], **27**, 465.

have the same percentage composition and that the simplest formula for both is the same, the next step was naturally the determination of the molecular weight of paranthracene, so that we might know whether anthracene and paranthracene were isomers or polymers. The molecular weight of anthracene has been determined many times by the vapor-density method as well as by the freezing- and boiling-point methods, so that its formula is known beyond a doubt to be $C_{14}H_{10}$. The vapor-density method of determining molecular weights is inapplicable in the case of paranthracene because this substance is transformed into anthracene at its melting-point (244°), while the freezing-point method gives such doubtful results, owing to the great insolubility of the material in all the solvents tried that it is also out of the question. The only method which offered any promise of success was the boiling-point method. In determining the molecular weight of paranthracene by this method we used the apparatus already described by us,[1] with ethylene bromide, pyridine, anisol, and phenetol as solvents. Owing to the slight solubility of the substance considerable difficulty was at first experienced in getting the paranthracene into such a form that it dissolved quickly in the solvent. After trying many methods we finally hit upon the plan of making the little tablets so porous and brittle that they broke into fine powder as soon as they came in contact with the boiling liquid and thus presenting a large amount of surface to the action of the solvent, dissolved immediately. To accomplish this we ground the paranthracene with alcohol to a pasty mass, which was then pressed into the shape of the ordinary tablets taking care to use as slight a pressure as possible. The tablets were then heated to 100° in an air-bath till they ceased to lose weight. In the following determinations we used paranthracene that had been crystallized at least three times and generally that which had been crystallized four times. The thermometer, which was of the Beckmann type and graduated in hundreths of a degree, was read by means of a telescope and the results were never calculated until all the readings had been taken. In every case a series was made according to the method of

[1] This Journal, 17, 517.

Beckmann. The following are the results obtained with ethylene bromide:

Paranthracene, $C_{14}H_{10} = 178$; $C_{28}H_{20} = 356$.

Solvent: Ethylene bromide,[1] ($C_2H_4Br_2$), boiling at 128.8° at 741.7 mm. Molecular rise for 100 grams 63°.2.[2]

Grams solvent.	Grams substance.	Observed rise.	Barometer. mm.	Mol. weight found.
195.69	0.1688	0°.030	743.0	179
"	0.3258	0°.055	743.0	188
190.55	0.2569	0°.035	736.4	243
"	0.3905	0°.051	736.4	253
176.06	0.1223	0°.014	738.2	314
"	0.2407	0°.025	738.1	346
184.22	0.2071	0°.020	734.7	353
"	0.3443	0°.040	734.7	295
181.25	0.1770	0°.018	737.3	343
"	0.3371	0°.035	737.3	336

Average of all determinations in ethylene bromide, 285

The results obtained by this method with ethylene bromide, it will be seen, are but little, if any, better than those obtained by Elbs in naphthalene by the freezing-point method. Six out of the ten values found indicate that paranthracene has a molecular weight of 356, and the average of all the determinations in ethylene bromide indicates the same fact, but the material is so slightly soluble in this solvent that the observed elevations of temperature are necessarily small. An error of observation in the hundreths place will frequently change the molecular weight from that required by a single molecule to that of a double molecule, or *vice versa*. We give these results here simply for the sake of completeness and because *at first* we were inclined to think that paranthracene was an isomer[3] and not a polymer of anthracene. It was quite evident from the above determinations that a solvent must be found which would dissolve more of the paranthracene than ethylene bromide if any decisive results were to be obtained. After much time and labor we found in pyridine, anisol, and

[1] The ethylene bromide was carefully dried with calcium chloride and purified by many distillations till it had a constant boiling-point.

[2] This is the constant obtained by Beckmann and confirmed by us. See this Journal, 17, 526.

[3] See *ante*.

phenetol, the solvents needed. The following are the determinations made with these liquids:

PARANTHRACENE, $C_{14}H_{10} = 178$; $C_{28}H_{20} = 356$.

Solvent: Pyridine[1] (C_5H_5N); boiling-point 114.2° at 741.7 mm. Molecular rise[2] for 100 grams 26.90.

Grams solvent.	Gram substance.	Observed rise.	Barometer mm.	Mol. wt. found.
97.88	0.3147	0°.024	733.3	356
"	0.6111	0°.048	733.3	350
"	0.8886	0°.077	733.3	317
88.49	0.2366	0°.020	737.2	361
"	0.3976	0°.036	737.2	338
"	0.6469	0°.056	737.2	352
92.62	0.1788	0°.014	747.7	371
"	0.4526	0°.034	747.6	387
"	0.6687	0°.054	747.6	360

Average of all determinations in pyridine, 354.

Solvent: Anisol,[3] ($C_6H_4O.CH_3$); boiling-point 152.7° at 741.7 mm. Molecular rise[4] for 100 grams 44°.3.

Grams solvent.	Grams substance.	Observed rise.	Barometer mm.	Mol. wt. found.
93.76	0.2739	0°.036	747.8	357
"	0.4956	0°.067	747.8	348
"	0.7011	0°.093	747.8	354
"	0.9012	0°.117	747.9	362
87.64	0.2610	0°.040	744.2	331
"	0.4960	0°.070	744.2	359
"	0.7212	0°.107	744.2	341
"	0.9671	0°.133	744.2	379
92.67	0.3655	0°.048	734.3	364
"	0.6350	0°.081	734.3	375
92.50	0.2279	0°.030	752.0	361
"	0.4958	0°.060	752.0	386
"	0.8236	0°.096	752.0	397

Average of all determinations in anisol, 362.

[1] The pyridine here used was a remarkably pure specimen, made from pyridine (marked C. P.) by boiling with solid caustic potash and rectifying till it was free from water and possessed a constant boiling-point.

[2] The molecular rise calculated from the absolute boiling-point according to the equation $K = \frac{0.0198\ TM}{20.8}$ was 29.°4, but the mean of seven determinations gave 26.90 which is the value used. See This JOURNAL, 17, 526.

[3] The anisol used was made by the action of methyl chloride on sodium phenolate and was carefully purified by many distillations until it had a constant boiling-point.

[4] In this case $K = \frac{0.0198 \times 427°.3 \times 108}{20.81} = 44°.4$ which agrees very well with the constant determined experimentally. See This JOURNAL, 17, 527.

Solvent: Phenetol,[1] ($C_6H_5OC_2H_5$), boiling at 167°.9 at 741.9 mm. Molecular rise[2] for 100 grams 49°.3.

Grams solvent.	Grams substance.	Observed rise.	Barometer mm.	Mol. wt. found.
77.34	0.1619	0°.028	743.8	366
"	0.3920	0°.070	743.8	355
"	0.7422	0°.126	743.8	373
"	1.0522	0°.168	743.9	396
82.64	0.2448	0°.042	745.5	346
"	0.4508	0°.080	745.5	335
"	0.6034	0°.109	745.5	329
"	0.8292	0°.144	745.5	342

Average of all determinations in phenetol, 355.

Average of 30 determinations in pyridine, anisol and phenetol: 357.

From these results with pyridine, anisol and phenetol we must conclude that paranthracene has double the molecular weight of anthracene, and that its formula is $C_{28}H_{20}$, a result in complete accord with that obtained by Elbs. It would be preferable therefore to call paranthracene *dianthracene* and thus do away with the prefix para, which now has no meaning here and is simply misleading. Moreover, this method of naming the substance shows at once just what it is, and indeed is already in general use as is shown by such names as dipyridine, dipicoline, diquinoline, diterpene, etc., etc.

An interesting question here suggests itself regarding this change of anthracene into dianthracene, namely: is this peculiar transformation characteristic of anthracene or is it also found in the derivatives of this hydrocarbon and in other hydrocarbons. In order to answer this question solutions of anthraquinone, dihydroanthracene, dichloranthracene and anthranol were exposed to the action of sunlight for some weeks. In none of these solution was any change noticed except in the case of anthranol which first turned green, then yellow, a white crystalline material separating out, very different in appearance from anthranol. On evaporating off the solvent (benzene) a nearly white product was obtained which turned brown and melted not very sharply at 265°–270° C., evidently

[1] The phenetol used was a very pure specimen which was carefully purified and subjected to quite a number of distillations before being used.

[2] This constant was experimentally determined. See This JOURNAL, 17, 528.

undergoing some sort of decomposition. This substance was less soluble in the ordinary solvents than anthranol and was completely insoluble in solutions of the alkalies even on long boiling. From its high melting-point (anthranol melts at 163°–170°, according to Liebermann), slight solubility and method of formation this substance would seem to be dianthranol, a dihydroxyl derivative of dianthracene, though further work must be done to show whether this view be correct or not. Unfortunately none of the higher homologues of anthracene were obtainable so that it is not possible to state whether they would polymerize in the same way as anthracene or not. Solutions of *pure* phenanthrene, retene, camphor and phenylacridine were also found to suffer no change in the sunlight, so that the transformation would seem to be due to some peculiarity of the anthracene molecule. Of all the substances which bear any relation to anthracene perhaps acridine, $C_{13}H_9N$, resembles anthracene most closely. This was shown very strikingly when solutions of acridine were exposed to the direct action of the sunlight. A light yellow crystalline coating formed on the sides of the bottles as in the case of anthracene solutions. This substance was exceedingly insoluble in all solvents tried, did not unite with acids to form salts as acridine does so readily, and on heating slowly to 250° volatilized without melting, the volatilized portion melting at the melting-point of acridine, dissolving in acids with the characteristic greenish fluorescence and exhibiting all the other properties of acridine. Heated rapidly the insoluble product melts at 276°, the melted mass after solidification melting at 107° (the melting-point of acridine), and showing all the other characteristic properties of acridine. This insoluble acridine is also converted into acridine by boiling for a long time in liquids in which it is slightly soluble. No further work was done with this substance, as its insolubility rendered purification impossible and even if it could be purified there is no way of determining its molecular weight. Whether this substance be diacridine and whether it be identical with the product obtained by Graebe and Caro[1] by the action of sodium amalgam on an alcoholic solution of acridine

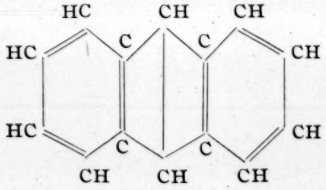
[1]Ann. Chem. (Liebig), **158**, 278.

and called by them insoluble hydroacridine,[1] remains an open question.

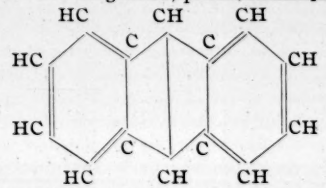
It is perhaps worth while to note here that Bernthsen and Bender found[2] that phenylacridine when reduced with sodium amalgam in alcohol did not give an insoluble compound analogous to the so-called insoluble hydroacridine of Graebe and Caro. This agrees with the observation made by us that phenylacridine solutions undergo no change in the sunlight analogous to that noted in the case of acridine itself.

THEORETICAL.

In order to express the relation existing between anthracene and dianthracene by structural formulas it will be necessary first to discuss the various formulas that have been proposed for anthracene and determine which one of these best represents the facts. The formula in general use



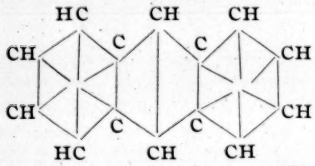
is one that was first proposed by Graebe and Liebermann in their celebrated paper on anthracene and alizarin. This formula is the one found in most text-books and is the one most generally accepted, though a second formula proposed by Behr and Van Dorp, and given by Seelig in his book *Organische Reactionen und Reagentien*, p. 620, is also possible:



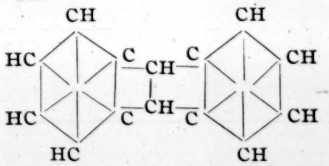
[1] For another suggestion regarding the structure of this substance, see Ber. d. Chem. Ges. **16**, 1973.

[2] *Ibid.* **16**, 1972.

The so-called quinoid formula of Armstrong, the prism formula of Wegscheider, and the centric formula of Bamberger for anthracene are not here considered as they do not represent the chemical conduct of anthracene as well as the other formulas which have been proposed. Besides these two formulas there is a third, which has not yet been proposed, so far as we are aware, for anthracene, but which we think is preferable to the other two:



or,



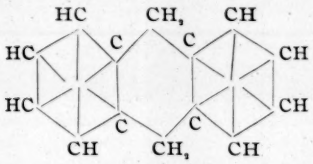
It is merely the application of the idea of centric bonds to the anthracene molecule, but should not be confused with the formula suggested by Bamberger.[1]

von Baeyer has shown that in benzene and the carboxylic acids derived from it the centric formula best represents the relation of the atoms. One of the principal reasons for this view is the extraordinary stability of benzene particularly towards oxidizing agents, such a powerful reagent as an alkaline solution of potassium permanganate having no action on this hydrocarbon. Now anthracene yields on oxidation anthraquinone, a substance which is especially characterized by its stability towards the most powerful oxidizing agents. In this oxidation of anthracene to anthraquinone neither of the benzene rings is affected, the so-called meso ring being the one that undergoes the change. Anthraquinone may be made from benzoic acid or phthalic acid and yields benzoic

[1] Ann. Chem. (Liebig), 257, 52.

acid when fused with solid caustic potash at a comparatively high temperature. Anthracene itself may be made synthetically from benzene and symmetrical tetrabrommethane, and that it contains two benzene residues must be accepted from this and other considerations. It seems highly probable, therefore, that if the centric formula be regarded as the correct representation of the condition of the atoms in benzene, benzoic, and phthalic acids, it must also be accepted for the benzene residues in anthraquinone and consequently in anthracene itself.

When anthracene is reduced in alcoholic solution by means of sodium amalgam it yields very readily dihydroanthracene, a substance which can be further reduced only by the action of the most powerful reducing agents, such as hydriodic acid and phosphorus. In this respect it will be seen that dihydroanthracene closely resembles benzene itself, as we should naturally expect if it were made up of two benzene residues united by two CH_2-groups as represented in the formula

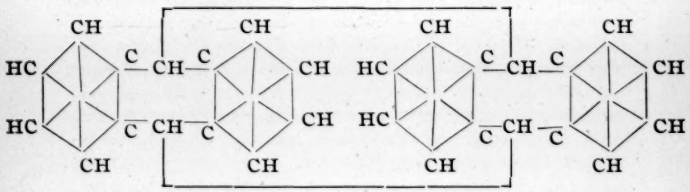


This centric formula for anthracene is, further, in accord with the fact that it is the γ-carbon or hydrogen atoms that are almost invariably the ones first affected when this hydrocarbon is acted on by the various reagents, the only exception being in the case of the action of sulphuric acid, which substitutes two of the benzene hydrogen atoms by sulphonic-acid groups—conduct in entire accord with the idea that the meso ring is made up of a paraffin residue which should not be affected by sulphuric acid.

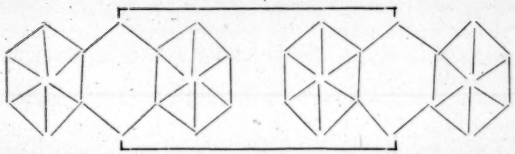
It will be seen on examining the formula proposed for anthracene that it represents that molecule as made up of two benzene rings, and two meso rings of four carbon atoms having two of these carbon atoms in common, and not as composed of three

benzene rings as usually stated. This will explain the difference in chemical conduct between this hydrocarbon and its isomer, phenanthrene, which actually does contain three rings of six carbon atoms.

When anthracene is either oxidized or reduced it yields readily compounds containing two benzene rings and one middle ring of six carbon atoms. As the tendency of carbon compounds to form rings containing six carbon atoms is very great this may explain why anthracene is so easily oxidized and reduced. Not only is this true but the fact that anthracene so readily polymerizes forming dianthracene, is also easily understood. For that dianthracene does not contain a para bond connecting the γ-carbon atoms must be assumed from the fact that it does not exhibit the fluorescence so characteristic of anthracene and its derivatives containing the para bond[1], and that it does not yield addition-products with chlorine or bromine nor with picric acid, as anthracene so readily does. It is quite probable, therefore, that the change of anthracene to anthraquinone, to dihydroanthracene, and to dianthracene are all due to the same cause: the presence in the anthracene molecule of the two middle rings of four carbon atoms and the general tendency so often noted in carbon compounds to form six-membered rings. The stability of anthraquinone towards oxidizing agents, of dihydroanthracene towards reducing agents, and of dianthracene towards reagents in general, thus receives a simple explanation. These considerations lead to the formula



[1] Liebermann: Ber. d. chem. Ges., 13, 913.



for dianthracene, very similar to the one suggested by Linebarger, though it will be observed that his statement that it contains a ring of four carbon atoms is erroneous. This formula is best represented by using solid models. Then, of course, the second half of the formula would be represented as superimposed on the first.

This formula for dianthracene will explain the transformation of this substance into anthracene under the influence of heat, the conversion of anthracene into dianthracene in the direct sunlight, the stability of dianthracene, and the fact that when it is acted on by reagents it gives derivatives of anthracene, being apparently first transformed into that hydrocarbon.

The crystallographic study of anthracene and dianthracene is also in accord with the formulas proposed for these substances. Assuming for anthracene the *trans* formula[1]

it will be noted by consulting the stereochemical model that it represents a monoclinic symmetry and anthracene crystallizes in the monoclinic system, as Koksharow has shown and as Dr. Gill has proved by a remeasurement of the crystals and a careful study of their optical properties. The stereochemical model of the dianthracene formula, on the other hand, represents an orthorhombic symmetry while dianthracene crystallizes in the orthorhombic system, according to the very careful measurements of Dr. Gill. The coincidences noted and enumerated by him between the anthracene and dianthracene crystals on the supposition that dianthracene is derived from anthracene by molecular twinning are also very

[1] The dotted line represents the hydrogen atom below the plane of the paper, the unbroken line the one above.

striking, and receive a ready explanation on the assumption of the above formulas. The specific gravity of anthracene and dianthracene are also in accord with these theoretical considerations.

The only other substances which were found to undergo a similar transformation to that observed in the case of anthracene were anthranol and acridine. To be sure it was not possible to determine whether the insoluble acridine was diacridine and that the change was strictly analogous to that of anthracene into dianthracene; still it is significant that both anthracene and acridine contain a "para" bond and both yield insoluble modifications when their solutions are exposed to the action of the direct sunlight. Whether the substances obtained from pyridine and quinoline by the action of sodium and called dipyridine and diquinoline, are similar in structure to dianthracene and whether their formation is due to the para bond in pyridine and quinoline remains yet to be proved; but there would seem to be no reason against such a supposition. It is to be noted in this connection that substances which do not contain a para bond, like anthraquinone and dihydroanthracene, suffered no change in the sunlight. Phenanthrene, too, isomeric with anthracene, undergoes no change when its solutions are exposed to the action of the sunlight.

The polymerizing action of light appears to have been but little studied and to have been observed only in connection with the polymerization of unsaturated compounds, if we except the observation that maleic acid is transformed into its isomer, fumaric acid, in the presence of a trace of bromine and in the sunlight.

A solution of sulphur or phosphorus in carbon bisulphide undergoes a change in the direct sunlight very similar to that observed in the case of solutions of anthracene. An insoluble modification is precipitated from the solution and the emergent light is destitute of the ultra-violet rays, while the less refrangible luminous part of the spectrum is unaltered. Apparently here the chemical rays are absorbed and expended in the production of chemical work. Whether the insoluble sulphur and the red phosphorus are polymeric modifications

of the ordinary sulphur and phosphorus can only be conjectured at present.

In the case of anthracene the change would seem to be closely connected with the strong absorption-bonds observed by Hartley in its solutions and with the fluorescence of this substance. Solutions of acridine and anthranol also show a bluish fluorescence in reflected light, and it would be interesting to compare the absorption-spectra of anthracene, dianthracene, anthranol, dianthranol, acridine and the insoluble acridine with reference to this subject.

Further work with a view to preparing derivatives of dianthracene will be undertaken in this laboratory.

Contributions from the Laboratory of Analytical Chemistry of the University of Michigan.

ON THE OXIDATION OF SOME GASES WITH PALLADINIZED COPPER OXIDE.

BY E. D. CAMPBELL.

In the work heretofore done on the combustion of gases where the well-known influence of finely divided palladium upon the ignition of gases has been taken advantage of, the oxygen for the combustion of the gas under examination has been introduced either as pure oxygen or diluted with nitrogen in the form of air. It was thought not impossible if palladium in sufficiently fine form and evenly distributed could be introduced into a solid reagent capable of giving up oxygen to combustible gases, that the temperature at which gases containing hydrogen would burn, might be lowered below the combustion-point in the absence of palladium, and that the differences in the temperatures of combustion of various gases might lead to a system of fractional combustion.

Copper oxide, being one of the most common reagents for combustion and having the great advantage over most others of being easily reoxidized after reduction, was thought to be the most desirable substance to work upon. Copper oxide containing palladium very finely divided and evenly distributed throughout, was prepared in three ways; of these the first by which the oxide used in the combustion shown in the table was made, was as follows:

An alloy was prepared by melting 600 grams of fine copper and then adding 6 grams of palladium. After melting, this alloy was cast into a cold iron mould, then broken up and re-melted at a temperature nearly approaching the melting-point of palladium (considerably above that of copper), then quickly recast into cold iron moulds, the strips so cast being about 12 mm. wide and 5 mm. thick. Palladium did not seem to alloy very readily with copper, so that it was necessary to re-melt at a high heat and cool quickly to prevent the palladium from distributing itself in the form of a fine network, which rendered the alloy brittle when attempts were made to roll it. By re-melting at a high heat and quickly cooling an alloy was produced in which the palladium was evenly distributed and which rolled as easily as pure copper. The strips of alloy thus produced were annealed like pure copper, then rolled until the thickness was reduced to 0.3 mm., the width remaining about the same. These strips were then cut transversely into pieces 1.5 mm. wide, thus giving small pieces 12 mm. long, 1.5 mm. wide, and 0.3 mm. thick. About 160 grams of this alloy was introduced into a combustion-tube of 16 mm. internal diameter, the alloy being retained in position at both ends by plugs of copper gauze. The column of alloy was 34 cm. long. The combustion-tube so prepared was placed in an ordinary Bunsen combustion-furnace, brought to a moderate red heat, and purified oxygen passed through as long as it was taken up.

Second Method.—In the course of the work, owing to frequent reduction and re-oxidation of the copper and to handling of the oxide in filling or emptying tubes, a considerable amount of fine oxide accumulated which could not be used as it was without choking the tube. This fine oxide was ground until it would pass through a 100-mesh sieve, mixed with thick mucilage to a rather stiff paste and pressed by means of a sodium press into wire a little less than 2 mm. in diameter. This wire, after it had become dry, was broken into pieces about 10–12 mm. long, introduced into a platinum crucible and heated to a moderate red heat until all volatile matter ceased coming off. The wire so produced was strong enough to retain its form perfectly while introducing it into a

combustion-tube in which it could be completely oxidized by means of oxygen at a red heat.

Third Method.—This method was not worked out until the combustions shown in the table were completed, but it is recommended as the best method for the purpose of preparing the oxide, as it is much simpler than either of the previous methods, and the oxide prepared by it we have shown by quantitative combustion of hydrogen is fully as efficient as that produced by the first or second method. The method is as follows: 3 grams of palladium wire was dissolved in a moderate-sized casserole by means of 40 cc. of nitric acid (sp. gr. 1.42) to which was added 10 cc. of hydrochloric acid (sp. gr. 1.20). After evaporating to dryness on the water-bath the palladium was brought into solution with 10 cc. of nitric acid, 3 cc. of hydrochloric acid and sufficient water to bring the volume to 60 cc. Into this solution was introduced 300 grams of pure copper oxide, previously ground to pass through a 100-mesh sieve. This produced a very stiff paste, which after thorough mixing was dried at 120° and again ground to pass through a 100-mesh sieve. The fine ground oxide so produced was then mixed with mucilage, pressed into wire, dried and ignited like that in the second method of preparation.

In order to control the temperature of the tube at any time a special form of air jacket was made, in two halves, so that it could be put on when the combustion-tube was used for combustion, or removed when it was desired to re-oxidize the copper without disturbing the position of the tube. The jacket consisted of two halves of a heavy brass tube 3 mm. thick, 52 mm. internal diameter, and 48 cm. long; this internal diameter allowed the jacket to surround the combustion-tube and its gutter and still leave a clear space of 5 to 7 mm., thus heating the tube entirely by radiation. The thickness of the inner brass tube also tended to equalize the temperature and to prevent sudden variations. The two halves of this inner brass tube were joined at both ends to an outer heavy sheet-iron tube, leaving between the tubes an annular space of 7 mm. The two halves of outer sheet-iron tube came together on the under side in the form of a lap joint and were

prolonged on the upper side so as to be supported by means of metal pins on both sides of the double horizontal bar at the top of the furnace usually used to keep the tiles apart. Through the double bar at the top of the furnace and through three holes in the inner brass tube, were introduced three nitrogen-filled thermometers capable of registering 460°. These thermometers reached to and rested on the inner combustion-tube. In addition to this jacket on each side of the furnace were provided two sheet-iron guards to prevent currents of air and to maintain a steadier heat. In addition to these a heavy sheet-iron gutter 54 mm. wide and 48 cm long, was curved to fit the under side of the outer jacket and when wired to it could take the direct heat of the flame and prevent the burning out of the outer jacket. This gutter was found necessary when working at the higher heats. Thus provided, the inner combustion-tube was so placed that it was heated by radiation from the heavy inner brass tube which was in turn heated by radiation from the outer sheet-iron jacket. In this way a steady, even temperature of the combustion-tube could be maintained at any temperature up to 450°, and the entire jacket could be easily removed, the tiles put back in their usual place and the copper reoxidized without disturbing the combustion-tube.

In determining the initial combustion-point of any gas a moderate flow of the pure gas was kept passing through the combustion-tube, to the farther end of which was attached a small tube containing glass-wool sprinkled with anhydrous cupric sulphate, for the detection of moisture, followed by a U tube containing a clear solution of calcium hydrate for the detection of carbon dioxide. The temperature of the tube was gradually raised, the three thermometers being kept within a range of 5° until a test for moisture and carbon dioxide was obtained. As soon as this was done in any case the supply of gas was shut off and pure dry air drawn through the tube, the temperature allowed to fall below the ignition-point, the gas turned on again and the temperature again carefully brought up until a second test was obtained. In gases containing both carbon and hydrogen, a test for carbon dioxide was obtained always a little in advance of that for

moisture. This difference is probably accounted for by the greater sensitiveness of calcium hydrate for carbon dioxide than that of anhydrous cupric sulphate for moisture. In the table of results, the limits of temperature given include those at which distinct test for both moisture and carbon dioxide were obtained. In determining the ignition-point of a gas it was also found necessary to use the combustion-tube after it had been used for a quantitative combustion, since a freshly reoxidized tube was found to contain small amounts of palladious oxide, which gives up its oxygen very much more readily than the copper oxide and which would consequently make the ignition-point apparently much lower than its true value.

For the quantitative combustion of gases, the inlet end of the combustion-tube was connected to a T tube provided with a three-way stop-cock by means of which either the pure dry gas under examination could be introduced into the tube, or by reversing the cock pure dry air or oxygen could be drawn or forced through the tube for the purpose of sweeping forward the products of combustion or for reoxidizing the copper when desired.

In determining the rate of combustion of any gas the method was as follows: The tube filled with air was carefully brought up to the temperature at which combustion was to be made and maintained at this temperature until thoroughly heated through. A weighed calcium-chloride tube was attached to the outlet of the combustion-tube, followed by a double Liebig potash-bulb. The latter was made by uniting two ordinary Liebig bulbs and placing in the first bulb a solution of potassium hydroxide (1 : 2), and in the second bulb a stronger (1 : 1), the bulb being provided with the usual guard-tube. It was found necessary to have the potassium hydroxide in the first bulb more dilute than 1 : 1, since most of the carbon dioxide was taken up in the first small bulb, and if 1 : 1 potassium hydroxide was used potassium acid carbonate crystallizes out so as to choke the tube. By using the more dilute solution in the first bulb the trouble is avoided. When the combustion-tube has attained the desired temperature, the pure gas under examination was forced through

the tube, the rate at which it is supplied being so regulated that as light excess of unburned gas passes completely through the train. In the combustions shown in the table this excess of unburned gas was judged by the number of bubbles passing through the last small bulb of the potash bulbs, and the supply of gas was so regulated that this excess should come through at the rate of 6–10 bubbles per minute. The exact time at which the gas was introduced into the combustion-tube was noted. The gas at the commencement was introduced rather rapidly for a few moments to expel the air in the tube, then the flow regulated to the 6–10 in excess and kept up for times varying from 45 minutes to 6 hours, according to the rate at which the gas burned. At the end of an exact time, the stopcock was reversed and pure air drawn through the tube until all the products of combustion had been collected. From the weight of water and of carbon dioxide or of both obtained, the number of cc. of pure gas required to produce these was calculated. In addition to the number of cc. of each gas burned per hour has been calculated the weight of oxygen removed from the copper oxide for the combustion. In order to determine the extent to which palladium effected combustion, the ignition-point of the various gases was determined by passing the gas over a long plug of pure copper oxide made by oxidizing pure copper gauze. This copper oxide was contained in a combustion-tube of the same size and heated in the same way as the one containing the palladinized copper oxide. It will be noted that the ignition-point of hydrogen has been reduced about 95°, that of ethylene 75°, of propylene 50°, of isobutylene 40°, while that of carbon monoxide, as would be expected, has not been affected.

In the preparation of gases the following methods were used:

I. Hydrogen was prepared by the action of dilute sulphuric acid on pure zinc and purified by passing through potassium hydroxide (1:1), over dry potassium hydroxide, calcium chloride and phosphorus pentoxide.

II. Carbon monoxide was prepared by the action of strong sulphuric acid upon oxalic acid, the carbon dioxide being re-

moved with potassium hydroxide and the gas being then purified in the same way as the hydrogen.

III. Ethylene was prepared by the action of ethyl alcohol upon phosphorus pentoxide and purified by passing through strong potassium hydroxide and then over three towers of dry potassium hydroxide. It was found in the course of the work that if phosphorus pentoxide was used in the train that there was some polymerization with ethylene and that this tendency to polymerize increases with propylene and was so marked with isobutylene as entirely to prevent the use of phosphorus pentoxide. Ethylene produced from alcohol and sulphuric acid in the usual manner was found to contain so much carbon monoxide as to be unfit for this work, while that produced by the method used was shown by analysis to be practically pure.

IV. Propylene was prepared by carefully heating propyl alcohol and phosphorus pentoxide and purifying as in the case of ethylene. This method gives very nearly if not quite pure propylene.

V. Isobutylene was prepared by the action of isobutyl iodide upon alcoholic potash, the gas being collected over a 10 per cent. solution of common salt and then purified in the same way as ethylene and propylene. When an attempt was made to obtain isobutylene by the action of the corresponding alcohol upon phosphorus pentoxide, it was found the resulting gas contained only about 60 per cent. of isobutylene and 35 per cent. of butane.

VI. Methane was prepared by the action of methyl iodide on zinc-copper couple immersed in alcohol. It was purified by passing through strong sulphuric acid containing chromic acid and then through strong potassium hydroxide, followed by dry potassium hydroxide and phosphorus pentoxide.

VII. Acetylene was prepared by the action of calcium carbide on water. It was purified and dried by passing through strong potassium hydroxide and then over dry potassium hydroxide.

The details of the temperature and rate of combustion of the above gases, except acetylene, which does not oxidize perfectly to carbon dioxide and water, are shown in the fol-

lowing table. All rates of combustion have been calculated from the weight of water or carbon dioxide obtained to the cc. of pure dry gas, under standard conditions, which would be burned in one hour. Since these combustions were all made in the same sized tube and with practically the same amount of surface of copper oxide exposed the rates of combustion are comparable. Of course varying the size of the combustion-tube and with it the amount of palladinized copper oxide present would alter the absolute rates of combustion but would probably not effect the relative rates.

In the case of easily burned gases, like hydrogen and carbon monoxide, it is not found necessary to re-oxidize the tube after each combustion, but in the case of more difficultly burned gases this was found desirable, especially when burning at the higher temperatures and when the previous combustion had removed a good deal of oxygen.

Exp. No.	Gas.	Initial combustion point with palladium copper oxide.	Initial combustion point with pure copper oxide.	Temp. of combustion.	Length of time in hours.	Wt. H_2O.	Wt. CO_2.	cc. of gas burned per hour.	Wt. O_2 removed per hour.
1	H_2	80–85°	....	....	.	....	....	....	....
2	H_2	....	175–180°	....	.	....	....	....	....
3	H_2	....	....	115–120°	6	0.4808	....	99	0.0713
4	H_2	....	....	125–130°	6	1.295	....	266.4	0.1918
5	H_2	....	....	135–140°	6	1.974	....	406.2	0.2925
6	H_2	....	....	145–150°	6	3.544	....	729.2	0.525
7	H_2	....	....	165–170°	6	3.688	....	754.8	0.5435
8	CO	100–105°	....	....	.	....	....	....	....
9	CO	....	100–105°	....	.	....	....	....	....
10	CO	....	....	125–130°	6	....	0.669	56.4	0.0406
11	CO	....	....	135–140°	6	....	1.0215	86.1	0.062
12	CO	....	....	145–150°	6	....	2.313	196.7	0.1403
13	CO	....	....	155–160°	2½	....	2.101	425.1	0.3059
14	CO	....	....	175–180°	1½	....	1.7685	599.5	0.4292
15	CO	....	....	195–200°	1½	....	1.951	654.9	0.4734
16	C_2H_4	240–250°	....	....	.	....	....	....	....
17	C_2H_4	....	315–325°	....	.	....	....	....	....
18	C_2H_4	....	....	270–275°	2	0.0515	0.116	14.7	0.063
19	C_2H_4	....	....	295–300°	2	0.111	0.268	33.8	0.145
20	C_2H_4	....	....	325–330°	2	0.3215	0.815	103.	0.442
21	C_2H_4	....	....	345–350°	2	0.489	1.1725	148.5	0.636

Exp. No.	Gas.	Initial combustion point with palladium copper oxide.	Initial combustion point with pure copper oxide.	Temp. of combustion.	Length of time in hours.	Wt. H_2O.	Wt. CO_2.	cc. of gas burned per hour.	Wt. O_2 removed per hour.
22	C_2H_4	....	....	370–375°	2	0.565	1.3665	172.8	0.741
23	C_2H_4	....	....	395–400°	2	0.5985	1.4555	184.	0.789
24	C_2H_4	....	....	420–425°	2	0.742	1.830	231.4	0.993
25	C_2H_4	....	....	450–455°	1½	0.561	1.388	234.	1.004
26	C_3H_6	220–230°	....	....	.	....	....	....	....
27	C_3H_6	....	270–280°	....	.	....	....	....	....
28	C_3H_6	....	....	240–245°	2	0.0315	0.0475	4.	0.0257
29	C_3H_6	....	....	270–275°	2	0.0905	0.179	15.1	0.0972
30	C_3H_6	....	....	295–300°	2	0.2345	0.569	48.	0.3089
31	C_3H_6	....	....	320–325°	2	0.9505	2.332	196.5	1.265
32	C_3H_6	....	....	345–350°	2	1.265	3.092	260.5	1.6695
33	C_3H_6	....	....	370–375°	2	1.2505	3.0125	253.8	1.634
34	C_3H_6	....	....	395–400°	2	1.271	3.0765	259.3	1.668
	Iso.								
35	C_4H_8	270–280°	....	....	.	....	....	....	....
36	C_4H_8	....	320–330°	....	.	....	....	....	....
37	C_4H_8	....	....	270–275°	2	0.051	0.196	7.87	0.0755
38	C_4H_8	....	....	295–300°	2	0.185	0.559	28.57	0.2454
39	C_4H_8	....	....	320–325°	2	0.6765	1.8665	104.4	0.895
40	C_4H_8	....	....	340–345°	2	1.6495	4.036	254.8	2.186
41	C_4H_8	....	....	370–375°	¾	1.431	3.4775	588.6	5.059
42	CH_4	No combustion at 455°.							

In the above table all of the quantitative combustions were performed with palladinized copper oxide, prepared by the first method, the ignition-point only of the various gases being determined with pure copper oxide in order to determine to what extent the presence of 1 per cent. of palladium affected the temperature at which combustion commenced. In the calculation of the rate of combustion of ethylene and of propylene (experiments 18–25 and 28-34), the volume was calculated from the amount of carbon dioxide since, owing to the use of phosphorus pentoxide in one arm of the U tube used for collecting the water, there was slight polymerization, which made the amount of water a little higher than the true value. On the other hand, in the case of isobutylene (experiments 37–41) the rate of combustion was calculated from the amount of water produced, the U-tube being filled with calcium chloride

alone, thus avoiding polymerization. The solubility of isobutylene rendered the carbon dioxide a little in excess of the amount calculated for perfect combustion so that it was thought to be more accurate in this case to use the weight of water rather than that of carbon dioxide in calculating the rate of combustion.

In all of the gases on which quantitative combustions were made, although a slight excess of unburned gas was forced completely through the train, if the supply was slackened a little, perfect combustion took place and no unburned gas escaped. In the case of methane no combustion took place at 455°, and, as 460° was the limit to which nitrogen-filled thermometers could be carried, it was found necessary to lay aside the work so far as the paraffins go until suitable modifications to the furnace can be made by means of which such temperatures as may be necessary for the combustion of these gases can be obtained and controlled, when the work will be continued. After obtaining the temperature of ignition and rate of combustion of the ordinary gases occurring in the pure state, mixtures of these gases will be worked upon in order to determine if possible to what extent they may be separated by fractional combustion. The combustion of acetylene differs from that of any of the gases given in the above table, since this gas does not burn at once to carbon dioxide and water, but undergoes a series of rather complex decompositions which would render it incapable of being separated by fractional combustion. In attempting to determine the ignition-point of acetylene, the pure dry gas was passed through a tube containing palladinized copper oxide, having a small tube of anhydrous cupric sulphate attached to the farther end, followed by a U-tube containing calcium hydroxide for the detection of carbon dioxide. A steady flow of gas was kept up through the tube, which was very slowly heated; no apparent change occurred until a temperature of 225°–230 was reached, when the first test for moisture was observed, but no carbon dioxide. The flow of gas was kept up, the temperature of the tube being gradually raised until a temperature of nearly 300° was reached, when the tube was found to be choked up although no test for carbon dioxide had as yet been obtained. On re-

moving the combustion-tube from the furnace the paladinized copper oxide nearest the inlet of the tube was found to be filled for a distance of about 5 cm. with a heavy black deposit. The combustion-tube was refilled with fresh palladinized copper oxide prepared by the second method, heated to nearly 300° and acetylene once more turned through the tube and the temperature raised, when a test for carbon dioxide was obtained at 315–320°. On removing the jacket from the furnace a deposit similar to the first was observed, but not in sufficient quantity to choke the tube; this deposit was removed by heating the tube to a red heat and forcing in oxygen until everything was burned. After thus re-oxidizing the tube the jacket was replaced and the temperature raised to and maintained at 345°. Acetylene was turned into the tube at such a rate that 3–5 bubbles per minute passed through the last bulb of the weighed potash bulb used for regular quantitative combustion. This was kept up for two hours, when it was found that the water obtained weighed 0.3171 gram and the carbon dioxide 0.4834 gram. If combustion had been perfect to carbon dioxide and water, then the amount of water obtained should have been accompanied by 1.547 grams carbon dioxide instead of less than one-third this amount. On removing the jacket a deposit similar to the previous ones was observed which was removed by oxidation at a red heat. A second quantitative combustion was then made, the temperature being 395–400°. In this combustion the amount of water obtained was 0.4056 gram accompanied by 1.4753 grams carbon dioxide—a little greater ratio than the previous one. After removing the jacket the carbonaceous deposit was again removed by burning at a red heat and the water and carbon dioxide produced were weighed. This gave: water, 0.0521 gram and carbon dioxide, 0.7737 gram. From these results we see that when acetylene is passed through a tube of palladinized copper oxide at a temperature of 395–400° two-thirds of the carbon and eight-ninths of the hydrogen are oxidized to carbon dioxide and water respectively, while one-third of the carbon and one-ninth of the hydrogen remain in the tube in a form as yet undetermined.

In a combustion similarly conducted but with the tempera-

ture at 445°–450° the amount of water obtained in the same length of time was 0.6747 gram accompanied by 1.9486 grams of carbon dioxide, thus showing that while the rate at which dissociation took place increased with rise in temperature, oxidation did not seem to reach a higher limit than at 400°.

Credit is due Messrs. R. F. Flinterman, C. R. Rose and E. B. Hart for the care with which they have carried out the laboratory work of the above research.

ANN ARBOR, *July, 1895.*

NOTES ON LIMONENE AND ITS DERIVATIVES.

BY EDWARD KREMERS.

Rotatory Power of Limonene.

In the contribution on "Terpene und Aetherische Oele,"[1] containing a report of the specific rotatory power of a number of terpenes and derivatives, by Wallach and Conradi, the following values for $[\alpha]_D$ for the limonenes are given:

Dextrogyrate Limonene, + 106.8°;
Lævogyrate Limonene, — 105°.

About five years ago, while working on the interesting phases of isomerism manifested by the limonene group of "terpenes," now terpadines, I made the observation that the $[\alpha]_D$ of a freshly distilled limonene was 121.3°.[2] This determination was made upon the pure oil without a solvent. A few months later a chloroform-solution containing 18.74 per cent. of oil was observed to have a specific rotatory power of 106.01°. Still later the $[\alpha]_D$ of a chloroform-solution containing 22.34 per cent. of the same oil was 101.01°. Without the use of a solvent $[\alpha]_D$ was determined to be 103.23°.

The diminution of the rotatory power was accompanied by an increase in the specific gravity of the hydrocarbon. Although my data were very meagre at the time, I ventured to express this opinion: "It is apparent that chloroform has but slight influence on the rotatory power of limonene. The

[1] Ann. Chem. (Liebig), **252**, 145.

[2] Isomerie verhältnisse innerhalb der Terpenreihe—Inaugural Dissertation: Goettingen, 1890, p. 18.

increase of the specific gravity and the decrease of the rotatory power show that limonene changes slowly but perceptably upon standing."

Last summer Mr. Edward A. Mayer had occasion to fractionate carefully several pounds of commercial "carvene." As a result a considerable quantity of pure limonene, *i. e.*, as pure as it could be obtained from this source by fractional distillation, was obtained. With such material at our disposal it seemed desirable to ascertain what influence some of the more common solvents exert upon the rotatory power of this hydrocarbon. For this purpose the fraction boiling between 174.5°–175° was employed. Its specific gravity at 20° was 0.8456; its $[\alpha]_D$ was + 120.466, *i. e.*, without solvent.

The data compiled in the following tables make it readily apparent that the solvents employed—absolute and ordinary alcohol, chloroform and glacial acetic acid—diminish the rotatory power of limonene. In the case of absolute alcohol and chloroform the rotatory power of the limonene seems to diminish with fair regularity as the quantity of solvent increases. In the case of the glacial acetic acid no such regularity is apparent. The data obtained with ordinary alcohol are not sufficient to warrant any general statement, though here also the few data obtainable point toward the same conclusion.

A short table of physical constants, *viz.*, specific gravity and $[\alpha]_D$ for the fractions just below and just above the limonene fraction, has also been appended, because it shows what influence the other constituents of caraway oil have on the specific gravity and rotatory power of the limonene.

These tables were compiled by Mr. Edward A. Mayer from the data obtained by him shortly after the fractionation of the oil.

SOLUTION IN ORDINARY ALCOHOL.

Fraction.	Percentage of oil.	Sp. gr. at 20°.	a^1.	$[a]_D$.[1]
174.5–175°	10	0.8180	9°.159	111°.968
	20	0.8201	18°.517	112°.894
	30	0.8247	28°.131	113°.701.

[1] Throughout these tables the sign is +.

Solution in Absolute Alcohol.

Fraction.	Percentage of oil.	Sp. gr. at 20°.	α.	$[\alpha]_D$.
174.5–175°	10	0.7975	9°.046	113°.430
	20	0.8005	18°.241	113°.940
	30	0.8071	27°.716	114°.470
	40	0.8133	37°.600	115°.570
	50	0.8172	47°.500	115°.690
	60	0.8235	57°.500	116°.373
	70	0.8286	67°.700	116°.720
	80	0.8349	73°.660	117°.768
	90	0.8409	89°.331	118°.036
	100	0.8456	101°.866	120°.466

Solution in Chloroform.

	10	1.3801	15°.964	115°.673
	20	1.2873	29°.771	115°.633
	30	1.2081	42°.362	116°.844
	40	1.1445	53°.716	117°.335
	50	1.0827	63°.665	117°.604
	60	1.0273	72°.875	118°.230
	70	0.9769	81°.152	118°.672
	80	0.9335	89°.185	118°.209
	90	0.8928	95°.405	118°.733
	100	0.8456	101°.866	120°.466

Solution in Glacial Acetic Acid.

	10	1.0229	11°.814	115°.495
	20	0.9980	22°.696	113°.707
	30	0.9738	33°.202	113°.650
	40	0.9537	43°.395	113°.753
	49.881	0.9337	53°.547	114°.971
	60	0.9124	63°.695	116°.350
	70	0.8946	72°.668	116°.041
	80	0.8789	81°.796	116°.332
	90	0.8641	90°.866	116°.841
	100	0.8456	101°.866	120°.466
172.5–173°		0.8455	99°.483	117°.662
173 –173°.5		0.8453	100°.733	119°.168
173.5–174°		0.8446	101°.189	119°.807
174 –174°.5		0.8443	101°.883	120°.672
174.5–175°		0.8456	101°.866	120°.466
175 –175°.5		0.8486	99°.273	116°.984
175.5–176°		0.8507	97°.887	116°.242
176 –177°		0.8536	97°.275	113°.958

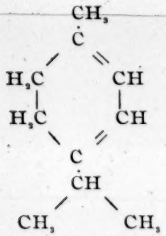
Terpin Hydrate from Limonene Monohydrochloride.

While engaged in the study of limonene and its derivatives, I made the observation that the fickle monohydrochloride of this "terpene" when in contact with water in a sealed tube in the course of time is converted into terpin hydrate, at least the appearance of the crystals as well as the transparency of the reaction seemed to justify this assertion. That it was justified I have recently determined by taking the melting-point of the crystals. When heated slowly they began to melt at 103° and were completely liquified at 116°. The contents of the tube, which had been heated considerably above the melting-point of terpin hydrate, after congealing melted completely at 103°, thus showing that it had been converted into anhydrous terpin.

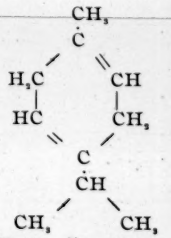
It may not be without interest to state that for more than three years the crop of crystals constantly though very slowly increased and that the monohydrochloride remained practically colorless. Then by accident the tube was broken; the oil became colored and ultimately dark brown, while at the same time the crystals were gradually redissolved by the mother-liquid. I mention this in case some one should desire to prepare terpin hydrate from limonene monohydrochloride.

On the Constitution of Limonene.

Prof. O. Wallach and Prof. A. v. Baeyer have both within the past year discussed the constitutional formula of limonene. The following formulas, which differ only with reference to the position of one of the two double bonds, have been suggested and arguments pro and con have been discussed.

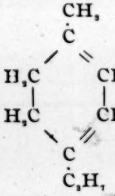


I.—$\Delta^{1,3}$ Terpadine.

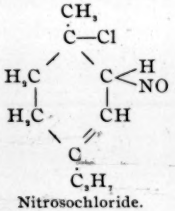


II—$\Delta^{1,4}$ Terpadine.

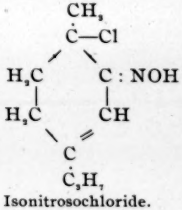
The older formulas, which gave an assymmetric carbon atom to limonene on account of its optical activity were unsatisfactory because they did not admit primarily of a satisfactory explanation of the conversion of limonene into carvone. In the recent discussions this reaction seems to have been ignored entirely. It may, therefore, not be out of place to call attention to the fact that formula I. admits of a very simple explanation of this reaction. The carvone formula to which it leads is that recently suggested by v. Baeyer. This reaction, therefore, has attained a double significance. It seems to ratify v. Baeyer's first formula for limonene as well as his formula for carvone. On account of this simple explanation, expressed by the following formulas, the writer favored formula I. even before v. Baeyer suggested the same, who assigned formula II. at that time to terpinene.



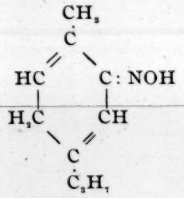
Limonene.



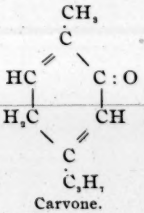
Nitrosochloride.



Isonitrosochloride.



Carvoxime.



Carvone.

These reactions are perfectly analogous to those which have been studied in connection with menthene nitrosochloride and which have lead to Δ^4 Terpene-3-one. Similar reactions are now being studied in connection with pinene nitrosochloride. In this case, however, a rearrangement of the

double, or rather para, bonds takes place and the expected ketone is converted into a phenol.[1]

PHARMACEUTICAL LABORATORY, UNIVERSITY OF WISCONSIN.

Contribution from the Kent Chemical Laboratory of the University of Chicago.

ON THE ACTION OF BROMINE ON METANITRANILINE.

BY H. L. WHEELER.

The action of the halogens on metanitraniline has been investigated only in a hydrochloric-acid solution: Körner[1] prepared *s*-tribrommetanitraniline by saturating the aniline with bromine in a dilute acid solution. Wurster and Nölting[2] state that they did not obtain a pure product in this manner. I have repeated the work of Körner and have found that the product formed in largest amount, by the action of bromine in a hydrochloric-acid solution, is *s*-tribrommetanitraniline, even when the operation is performed in the cold and in the presence of an excess of metanitraniline. Similar results were obtained when the nitraniline was dissolved in concentrated sulphuric acid, one molecule of bromine added and the mixture heated to 130° in a sealed tube. Bromine in cold concentrated sulphuric acid has little action on metanitraniline.

It is to be noticed that the behavior of metanitraniline, under the above conditions, is perfectly analogous to that of aniline.[3] It has been frequently observed that other meta substituted anilines behave like aniline where exposed to the action of the halogens. Nölting[4] called attention to this fact, as follows "Ueberhaupt verhält sich ein bei 3 substituirtes Anilin Agentien gegenüber gerade so wie ein gar nicht substituirtes." Later this idea was further developed by Langer.[5] He investigated the final action of chlorine and bromine on a number of substituted anilines and summarized the results in the form of the following law: "dass bei weiterer Substitution des

[1] See this JOURNAL, **17**, 607 *et seq.* [2] Jsb. 1875, 346.
[3] Ber. d. Chem. Ges. **7**, 1564. [4] Compare Hafner: *Ibid.* **22**, 2524.
[5] *Ibid.* **8**, 1093.
[6] Ann. Chem. (Liebig), **215**, 107; Ber. d. Chem. Ges., **15**, 1061, 1328.

Anilins solche Substituenten, die zur Amido gruppe die Metastellung einnehmen gar keinen bemerkbaren Einfluss ausüben und die Zahl der neu eintretenden Halogenatome nicht verringern."

It is to be noticed that these statements apply when the anilines are exposed to the final action of chlorine and bromine, since the work from which they were derived consisted in saturating the meta substituted anilines with chlorine and bromine. It has been found, however, in the case of metanitraniline that these generalizations do not apply under any other than the above mentioned conditions. In other cases, not only does the nitro group in the meta position exert a decided influence on the substitution of the aniline, but it also diminishes the number of halogen atoms that the non-substituted aniline is capable of taking up. Indeed even before the publication of Langer's observations, it had been shown by Michael and Norton[1] that a nitro group in the meta position diminishes the number of iodine atoms that the aniline when not substituted is capable of taking up. They found that aniline and iodine monochloride gave *s*-triiodoaniline while under the same conditions metanitraniline and iodine monochloride gave only diiodometanitraniline. These authors also found that iodine monochloride does not further substitute this di derivative even at 100°.

I have found that the nitro group exerts a protective influence on the aniline in regard to further substitution by bromine.[2] In the case of orthobrommetanitroacetanilide this substance can be crystallized unaltered from pure bromine. On the other hand acetanilide readily forms a dibrom derivative.

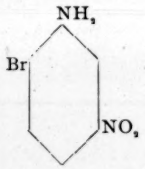
If metanitraniline is brominated, using the proper quantity of bromine, in a glacial acetic-acid solution, the chief product formed is a new monobrommetanitraline, $[NH_2, NO_2, Br: 1,3,6]$. The entering bromine takes the ortho position to the amido group. Under similar conditions aniline gives principally tri- and dibrom anilines. Moreover the mono derivatives

[1] Ber. d. Chem. Ges., 11, 112.

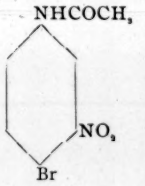
[2] This is most noticeable in the case of the acetyl compounds. On brominating metanitroacetanilide only parabrommetanitroacetanilide was formed and this gave no higher substitution-product with an excess of bromine.—This JOURNAL 17, 612.

formed, when the halogens act on aniline, according to Mills,[1] Kekulé[2] and Hofmann[3] are para and not chiefly ortho derivatives. Here it is evident that the nitro group, besides protecting the aniline, also influences the further substitution in another way.

The statement that a substituent in the meta position does not influence the further substitution of the aniline is not in harmony with the interesting observation of Kehrmann.[4] This author calls attention to the fact that when disubstituted benzenes are further substituted the entering substituent generally takes the ortho position to the substituent of least molecular magnitude. This is precisely what takes place in the case of metanitraniline: the free base gives orthobrommetanitraniline (I), while the acetyl compound yields only parabrommetanitroacetanilide (II).



I.



II.

I have recently shown[5] that when metanitroacetanilide is brominated the reaction takes place in two stages. In the first place a dibrom addition-product is formed; this then separates hydrobromic acid giving the so-called substitution-product. No such intermediate addition-product was observed when bromine was added to the free base. In this case *s*-tribrommetanitraniline and orthobrommetanitraniline hydrobromide were directly obtained.

Experimental Part.

Orthobrommetanitraniline, (NH_2,NO_2,Br : 1,3,6). — This new compound is formed on adding bromide to a solution of

[1] Ann. Chem. [Liebig], **176**, 355.
[2] Ztschr. Chem., 1866, 687.
[3] Ann. Chem. [Liebig], **67**, 61.
[4] Ber. d. chem. Ges., **23**, 130.
[5] This Journal, **17**, 612.

metanitraniline in glacial acetic acid, chloroform or benzene. The first mentioned solvent is most suitable. 1 molecule metanitraniline dissolved in glacial acetic acid and 1 molecule of bromine added, either in vapor form or slowly dropped in, produces a colorless shining crystalline precipitate. This consists chiefly of the hydrobromic-acid salt of orthobrommetanitraniline. After washing thoroughly with glacial acetic acid it is converted into the base by means of water and a little dilute ammonia, and this on crystallizing from alcohol is readily obtained pure. It then separates in the form of bright yellow needles melting at 139°–140°. A bromine determination was made by the method of Carius.

0.2638 gram substance gave 0.2262 gram AgBr.

	Found.	Calculated for $C_6H_4N_2O_2Br$.
Br	36.49	36.86

This substance gave with ethyl nitrite parabromnitrobenzene and, by means of Sandmeyer's reaction, dibromnitrobenzene (NO_2,Br,Br: 1,3,4). The structure is therefore: NH_2,NO_2, Br: 1,3,6.

Orthobrommetanitraniline dissolves readily in ether, chloroform, or benzene, less readily in alcohol, and difficultly in ligroïn and in water. From water long hairlike golden-yellow needles separate; these have a magnificent silky lustre. This substance is readily volatile in steam; its most characteristic property is its remarkable sweet-licorice taste, which can be detected in extremely dilute solutions.

It seemed of interest to determine whether the corresponding chlorine derivative [NH_2,NO_2,Cl: 1,3,6] had a sweet taste. This was prepared according to the method of Claus and Stiebel.[1] After purification, by means of ligroïn, which completely extracts the bitter bye-products, the chlorine derivative had the sweeter taste. This is probably due to its greater solubility.

Orthobrommetanitraniline is less basic than parabrommetanitraniline. Salts can be obtained by dissolving the substance in strong acids; these are decomposed by water.

The *hydrochloride*, $C_6H_3.NH_2.NO_2.Br.HCl$, crystallizes in

[1] Ber. d. chem. Ges., **20**, 1379.

colorless shining scales, which are difficultly soluble in concentrated hydrochloric acid. These melt with decomposition at about 200°.

0.2919 gram substance dried over sulphuric acid gave 0.1652 gram AgCl.

	Found.	Calculated for $C_6H_3.NH_2.NO_2.Br.HCl$.
HCl	14.39	14.39

The *sulphate*, $(C_6H_3.NH_2.NO_2.Br)_2.H_2SO_4$, crystallizes in beautiful colorless, shining, extremely thin, broad plates. These readily inclose some of the strong acid mother-liquor.

0.503 gram substance dried over sulphuric acid gave 0.272 gram $BaSO_4$.

	Found.	Calculated for $[C_6H_3.NH_2.NO_2.Br]_2.H_2SO_4$.
H_2SO_4	22.7	18.4

Orthobrommetanitroacetanilide.—This was obtained by boiling the glacial acetic-acid solution of the base for a half-hour with acetyl chloride and anhydrous sodium acetate. It is readily soluble in hot alcohol, difficultly in water. It crystallizes in beautiful, colorless, silky needles melting at 180°.

0.2717 gram substance gave 0.1948 gram AgBr.

	Found.	Calculated for $C_8H_7N_2O_3Br$.
Br	30.5	30.8

s-Tribrommetanitraniline, (NH_2, Br, NO_2, Br, Br: 1,2,3,4,6). This substance is found in the glacial acetic-acid filtrate when metanitraniline is brominated as indicated above. When this filtrate is diluted with about two volumes of water the tribromide is precipitated along with whatever resinous products have been formed. The precipitate, boiled with dilute alcohol and animal charcoal, gives, on filtering and cooling, pale yellow needles melting at 102°–103°.

0.2928 gram substance gave 0.4412 gram AgBr.

	Found.	Calculated for $C_6H_2N_2O_2Br_3$.
Br	64.12	64.00

This compound, as already stated, was obtained by adding bromine to a hydrochloric-acid and a sulphuric-acid solution of metanitraniline. The hydrochloric-acid solution as describer by Körner[1] is most suitable for its formation.

[1] *Loc. cit.*

s-Tribrommetanitraniline exhibits weakly basic properties. Salts cannot be prepared in the presence of water. They are very unstable and are readily decomposed on exposure to the moisture of the air. The hydrochloride is obtained by saturating a strong benzene solution of the base with dry hydrochloric acid gas. It crystallizes in colorless needles or prisms. The formation of the sulphate was observed when a mixture of 5 grams of metanitraniline, 50 grams of concentrated sulphuric acid, and 7.5 grams of bromine were heated in a sealed tube for eight hours to 120°–130°. On cooling the tube was filled with a mass of colorless needles. These were washed with concentrated sulphuric acid and finally with ether. Qualitative tests then proved that this was the sulphuric-acid salt and not the hydrobromide. On crystallizing the sulphate from alcohol *s*-tribrommetanitraniline was obtained. Ice-water precipitated more of the base from the sulphuric-acid filtrate. On account of the unstable nature of these salts they were not analyzed.

s-Tribrommetanitroacetanilide. — This compound was prepared in the same manner as given under the head of orthobrommetanitroacetanilide. On crystallizing from alcohol colorless prisms or stout crystals separated; these melted constantly at 169°. Concentrated nitric acid decomposes this substance with greater difficulty than the monobrominated aniline. A bromine determination was made according to the method of Carius, in which the substance was heated with nitric acid to 200°–250° for several days. This gave 2 per cent. less bromine than the calculated amount. Orthobrommetanitroacetanilide on the other hand was readily and completely decomposed by this treatment.

Orthobrommetanitraniline hydrobromide and *s*-tribrommetanitraniline are the chief products of the action of bromine on metanitraniline in a glacial acetic-acid solution. From 100 grams of metanitraniline 87.5 grams of crude orthobrommetanitraniline and 19 grams of tribrommetanitraniline were obtained, while about 30 grams of unaltered aniline were recovered. The metanitraniline was obtained after the removal of the tribromide, by adding ammonia to the diluted acetic-acid filtrate. The precipitate thus produced weighed 30.5

grams. On crystallizing from dilute alcohol it melted at 114° and was practically free from bromine. It therefore consisted chiefly of unaltered metanitraniline. The material in the mother-liquor from this amounted to only a few grams, it had a strong sweet taste and it also contained bromine. This material was probably a mixture of ortho and para monobrom derivatives with metanitraniline.

The alcoholic mother-liquor from the purification of orthobrommetanitraniline was evaporated to dryness, a little sulphuric acid was added and the whole distilled in steam. This removed the orthobrom derivative completely. The residue was filtered, dissolved in alcohol, concentrated hydrochloric acid was added and the whole evaporated to dryness. The residue was then extracted repeatedly with quite dilute hydrochloric acid, the solutions were united and precipitated with ammonia. On crystallizing the precipitate thus produced repeatedly form a mixture of benzene and ligroïn it melted finally at 130°. This was probably parabrommetanitraniline. A sufficient quantity of pure material was not obtained for satisfactory identification. The residue left undissolved by the hydrochloric acid, amounted to only a few grams; it consisted of what seemed to be a mixture of the dibrommetanitranilines. Experiments undertaken to separate these were without success.

An attempt to prepare the dibrommetanitranilines, by mixing the calculated quantity of bromine with the anilides dissolved in glacial acetic acid, resulted in a proportionally larger yield of mono- and tribrommetanitranilines. 10 grams metanitraniline dissolved in 100 grams of glacial acetic acid were treated with 23.2 grams of bromine in 25 grams of glacial acetic acid. This gave 11.1 grams of crude monobrom- and 10.7 grams of tribrommetanitraniline. On crystallizing the mono derivative from alcohol, 6.4 grams of pure substance were obtained.

It is my intention to investigate the action of bromine on propylmetanitraniline or on methylethylmetanitraniline. It is hoped in this manner to obtain results which will throw more light on the action which takes place when both metanitraniline and metanitroacetanilide are brominated. The

relative molecular magnitudes of the substituents in these anilines are the same as in metanitroacetanilide, but these compounds differ from metanitroacetanilide inasmuch as the groups $-N<^{H}_{C_6H_5}$ and $-N<^{CH_3}_{C_6H_5}$ are more basic than the group $-N<^{H}_{COCH_3}$. These compounds, like metanitroacetanilide, should give principally parabrom derivatives, if the process of bromination in each case is the same or if the position of the entering bromine atom is determined by the relative molecular magnitudes of the substituents. If on the other hand the basicity determines the position of the bromine atom, ortho derivatives would be formed, as in the case of the action of bromine on metanitraniline.

July, 1895.

A NEW REAGENT FOR BROMINE AND IODINE. PRELIMINARY NOTICE CONCERNING THE HALOGEN DERIVATIVES OF THE SULPHONAMIDES.

By J. H. Kastle.

Some months ago while working with *p*-chlorbenzenesulphonamide, a new bromine derivative of this substance was obtained by treating a caustic-soda solution of the amide with bromine water. The substance thus obtained was crystalline, yellow in color, possessed a slight odor of bromine and on analysis gave the following numbers:

		Calculated for $C_6H_4<^{SO_2NH_2Br_2}_{Cl(p)}$.
Br	45.53	45.51
N	3.80	3.98
S	9.70	9.10

An examination of the literature showed that no halogen derivative of the sulphonamides had ever been described. Several such derivatives of the carbonic amides, however, are well known, and by analogy the compound above mentioned ought probably to be regarded as of this nature: $C_6H_4<^{SO_2N.Br_2}_{Cl(p)}$, *i. e.*, as a dibrom substitution-product of the *p*-chlorbenzenesulphonamide in which the two bromine

atoms have replaced the two hydrogen atoms in the amide portion of the compound. That such really is the case, seems at the present writing to be open to doubt. Even in the case of similar derivatives among the carbonic amides, this structure seems open to question, and yet, apparently without much question, such a structure has been commonly assigned. For example, these formulas have been used repeatedly:

$CH_3CONHBr$; CH_3CONBr_2; $C_6H_5CONHCl$; $C_6H_5CONHBr$; $\begin{matrix}CH_3CO\\CH_3CO\end{matrix}>N.Cl$; in spite of the fact that in no instance, save possibly one, has any reaction of which they are capable seemed to show that the halogen atoms occupy the place of the hydrogen in the amide. In fact one of the most characteristic reactions of this class of bodies is that with various reagents—acids, alkalies, etc.—they yield the corresponding amides.

In his efforts to synthesize higher compounds of nitrogen through the aid of these derivatives Bender[1] failed, as did also later Linebarger,[2] "benzamide being the only crystallizeable compound obtained." I quote the latter's words concerning his results with the bromine derivative of benzamide, the formula of which is given as $C_6H_5CONHBr$.

In view therefore of the unsatisfactory condition of our knowledge concerning the nature of the halogen derivatives of acid amides, it was thought advisable to make a thorough study of this subject. The halogen derivatives of the sulphonamides being chosen as the substances best suited to this study in consequence of the ease with which they can be obtained in beautifully crystalline condition. A number of the di-halogen derivatives of several sulphonamides have been prepared, two of which, the dibrom and the dichlor derivatives of benzene sulphonamide are of remarkable beauty. The conduct of these substances towards a good many simple reagents has been studied. As in the case of the halogen derivatives of benzamide the amide itself seems to be the end-product of nearly all of these reactions, and yet the data at hand at present are hardly sufficient to enable one to reach a satisfactory conclusion concerning the structure of these substances.

[1] Ber. d. chem. Ges., 19, 2274.

[2] Linebarger: This JOURNAL, 16, 216.

Among the other transformations of which these derivatives are capable may be mentioned one which is most peculiar and interesting, and, so far as I am aware, entirely without a parallel among chemical reactions.

It is this: when the dichlor derivative of the benzenesulphonamide is heated to about 170°, it decomposes with evolution of chlorine, nitrogen and hydrochloric acid and gives almost the theoretical quantity of benzenesulphon chloride, a decomposition which is remarkable in many respects.

The Dichlor Derivative of Benzene Sulphonamide as a Reagent for Bromine and Iodine.

Among the other reactions of which it is capable, it was found that the dichlor derivative of benzene sulphonamide decomposes metallic bromides and iodides with the formation of the metallic chlorides and the corresponding brom and iodo derivatives of the amide; and it was further observed that when this decomposition was effected in the presence of carbon bisulphide or chloroform the latter solvents were colored yellow and violet just as they are with bromine and iodine.

The use of chlorine-water as a reagent in testing for bromine and iodine, is not altogether free from objections, not the least of which is, that at the moment when most needed a quantity of this reagent carefully prepared and placed in a dark closet will be found to have altered so that it is no longer a solution of free chlorine but one of hydrochloric acid, and hence of no use for this purpose.

The uncertain character of a bottle of chlorine-water has doubtless been the matter of an unhappy experience in the lives of most chemists. It was therefore deemed expedient to test this new compound as a reagent for bromine and iodine, the specimen used in these experiments being one which had been kept in this laboratory during the summer months in a loosely stoppered bottle.

The tests were made with the following solutions with the following results:

SOLUTIONS.

Solution I., containing 127 parts of iodine per million; made by dissolving 0.0166 gram potassium iodide in 100 cc. of water.

Solution II., containing 80 parts of bromine per million; made by dissolving 0.0119 gram potassium bromide in 100 cc. of water.

Solution III., containing 12.7 parts of iodine per million; made by making 10 cc. of Solution I. up to 100 cc. with water.

Solution IV., containing 8000 parts of bromine per million. Made by dissolving 1.19 grams of potassium bromide in 100 cc. of water.

No. of experiment.	Amount in cc. used. Solution. I.	II.	III.	IV.	Water.	Reaction for iodine.	Reaction for bromine.
1	5.0	....	....	....	....	Very decided.	.....
2	1.0	....	....	....	4.0	Good.	.....
3	0.5	....	....	....	6.0	Perfectly distinct.	.....
4	0.2	....	....	....	9.8	Distinct.	.....
5	0.5	10.0	....	....	....	Very distinct.	Good.
6	0.4	9.8	....	....	....	Distinct.	Distinct.
7	....	....	5.0	....	....	Good.	.....
8	....	....	1.0	....	....	Slight but distinct.	.....
9	...	5.0	5.0	....	....	Distinct.	.....
10	....	5.0	1.0	....	....	Distinct.	Distinct.
11	....	....	0.5	....	4.5	Slight but distinct.	.....
12	....	4.5	0.5	....	....	Distinct.	.....
13	....	....	2.0	5.0	....	Perfectly dist'ct.	Excellent
14	....	....	1.0	0.5	....	Distinct.	.....
15	....	....	1.0	5.0	....	Perfectly dist'ct.	Excellent

According to these results it is possible by the proper use of this new reagent to recognize 0.0000127 gram of iodine in the presence of 0.6400 gram of bromine; or 0.00000635 gram of iodine in the presence of 0.00036 gram of bromine.

My friend, Dr. A. M. Peter, chemist of the Agricultural Experiment Station here, was good enough to repeat some of the above experiments for me with results altogether similar to those above given. It is his opinion that as a reagent for iodine, the dichlor derivative of benzene sulphonamide is more satisfactory than potassium nitrite.

In the light of these results there can be no question as to the delicacy of this new compound as a reagent for bromine and iodine. I therefore propose its use for this purpose, and give the following method for its preparation: Benzene sulphonamide is dissolved in the smallest possible quantity of a

1 : 10 solution of caustic soda, and into this solution there is conducted a rapid current of chlorine. Under these conditions a white precipitate is produced by the chlorine, the first portions of which contain considerable quantities of the unchanged amide. This should be filtered out and the filtrate again treated with the gas. The second precipitate thus produced consists chiefly, if not entirely, of the dichlor derivative of the amide. It is filtered out of the solution and partly purified by heating with water and decanting. Under these circumstances the dichlor derivative, melting as it does at 70°, and being nearly if not entirely insoluble even in hot water, is separated from any of the original amide with which it is admixed as a light yellow oil, which solidifies when poured into cold water. In appearance and in many of its physical properties it resembles a solid acid chloride. It may be further purified by dissolving in absolute alcohol and adding a small quantity of water, which latter substance precipitates it in the form of white, lustrous, pearly plates.

In using the substance in testing for bromine and iodine it may be added either in the solid state or in solution in carbon bisulphide ; indeed in testing for very minute quantities of iodine it is preferable to use the carbon-bisulphide solution for the reason that smaller quantities of the reagent can thus be added to the solution containing the bromine or iodine. In this connection it must be borne in mind of course that in testing for very minute quantities of iodine it is necessary to add correspondingly small quantities of the reagent for the reason that, like chlorine, it reacts with the iodine set free to form the colorless iodine trichloride, and hence if care be not exercised, very small quantities of iodine may escape detection.

STATE COLLEGE OF KENTUCKY, *October, 1895.*

REVIEWS.

THE DISSOCIATION OF ELECTROLYTES AS DETERMINED BY SOLUBILITY-EXPERIMENTS.

Several papers have appeared during the past few years on the determination of the dissociation of electrolytes by means of solubility-experiments, and as the problem is now satisfactorily solved, it seems desirable to review the different papers

that have been published on this important subject. The first of these was published by Nernst,[1] and was on the mutual influence of salts on their solubility. He begins by showing how to calculate the amount of work that would have to be done against osmotic pressure in order to dissolve, at a fixed temperature, a gram-molecule of any substance in a solvent which is already saturated and constantly kept so, by proper addition of solvent, with the substance in question. The conclusion is that, where chemical action is absent, this work is independent of the nature, both of the dissolving substance and of the solvent. This is but the application of a well-known gas law to solutions, and at once suggests the application of other gas laws. Among these is the law that the amount of gas which a given space will contain, at ordinary pressure, is nearly independent of the presence of other gases which are neutral with respect to the one under consideration, and it is found that the same statement is applicable to solutions. Another gas law, of importance in this connection, is embodied in the statement that if any enclosed space be saturated with a gas which is known to dissociate, and if an additional amount of one of the dissociated parts be added, a corresponding amount of the original non-dissociated substance will separate out, while no change will take place on the addition of a neutral foreign gas. Thus, if a given space be saturated with ammonium chloride, which is known to dissociate into ammonia and hydrochloric acid, ammonium chloride will be deposited on the addition of either ammonia or hydrochloric acid, but no change will take place on the addition of a neutral gas, *e. g.*, nitrogen. This law was known to hold at least qualitatively in the case of solutions also, but Nernst tested it quantitatively by adding to saturated solutions of silver acetate known amounts of sodium acetate in one case and silver nitrate in another. Silver acetate was always precipitated from the solution to an extent corresponding to the amount of the sodium acetate or silver nitrate added. The relation between the quantities of the salts in solution was in fair accord with the formula, suggested by the above gas laws, $m(m+x) = m_0^2$, where m_0 is the number of gram-molecules per liter of the silver acetate in a saturated solution; x that of the sodium acetate or silver nitrate added; and m that of the silver acetate in solution after the addition of the silver nitrate or sodium acetate. The above formula assumes complete dissociation, an assumption which lowering of the freezing-point and conductivity-experiments show is not correct except for very dilute solutions. By allowing for this we obtain the corrected for-

[1] Ztschr. phys. Chem., 4, 372.

mula $m\alpha(m\alpha+x\alpha')=m_0^2\alpha_0^2$, where α, α' and α_0 are respectively the activity-coefficients, or percentages of dissociation, of m, x and m_0. This equation does not enable us to determine m in terms of known quantities, but as conductivity-experiments show that certain salts—potassium chloride, potassium bromide, sodium chloride, sodium acetate and others—dissociate to nearly the same extent in solutions of equal concentration, it is therefore natural to suppose that in such cases by taking $\frac{m}{m+x}$ cc. of the one salt solution and $\frac{x}{m+x}$ cc. of the other, where x and m are their respective concentrations, we should have $\alpha=\alpha'$ and consequently $m=-\frac{x}{2}+\sqrt{m_0\left(\frac{\alpha_0}{\alpha}\right)^2+\frac{x^2}{4}}$. This makes possible the calculation of m when α is known, or the reverse, since the other terms are all known. The few experiments described by Nernst agree well with this formula. Many persons had previously worked on the mutual influence of salts on their solubility, but without reaching any general law; probably because in most cases they worked with easily soluble salts which possibly modify the solvent and which give osmotic pressures amounting to hundreds of atmospheres—pressures at which ordinary gas laws do not hold.

The next paper on this subject is by Noyes,[2] who subjected Nernst's solubility-law to a number of careful tests and found it to hold in the main very well, though certain discrepancies between the values of m, as calculated by the formula and those found by experiment, lead him to question the values of α given by conductivity. He therefore undertook to determine the values of α in certain cases by means of solubility, which is possible by Nernst's formula as well as by the following equation, given by the law of mass-action, $m(1-\alpha)=m_0(1-\alpha_0)$. The former is used, which, of course, is assuming that the dissociations of the two salts concerned are the same, and Noyes therefore, apparently with good reason, assumed that under similar conditions, thallium salts, with which he worked, are dissociated to the same extent as the salts of the alkali metals. He was thus enabled to calculate for various concentrations the dissociation-constant, which for binary electrolytes is equal, from the law of mass action, to $\frac{1-\alpha}{n\alpha^2}$ where n is the number of gram-molecules per liter in solution. This he found by his experiments to be nearly a constant, which theory indicates it should be, even in places where conductivity gave it widely differing values, and so he

[2] Ztschr. phys. Chem., 6, 241.

concluded that dissociation can be determined more accurately by means of solubility-experiments than by conductivity.

This line of work was continued by Noyes[1] and the results were published in another paper which is chiefly a report of a large number of experimental determinations of dissociation by means of solubility, which method he still thought more reliable than that of conductivity.

Arrhenius[2] is next to take this matter up. He objects to the views of Noyes as they forced him to conclude that water is dissociated enough to play an important part in the conductivity of electrotytes, which is contrary to Hittorf's[3] investigations. Arrhenius therefore carried out a series of solubility-experiments himself, and from them calculated the dissociation on the assumptions that the non-dissociated part of the salt in solution is constant, at any given temperature, and independent of the presence of any neutral substance in the solution, and that the law of mass-action holds for electrolytes in solution—the law which conductivity renders doubtful for easily soluble salts, strong acids and strong bases, but which seems supported by Noyes' work. The values of the so-called dissociation-constant, $\frac{1-\alpha}{n\alpha^2}$, obtained in this way by Arrhenius, for different concentrations of a given salt in presence of another, differ widely and seem to depend in some way on the solubility of the second salt. Consequently Arrhenius claims that his second assumption, law of mass-action, does not apply to strongly dissociated electrolytes. The paper, however, is not conclusive, as Noyes states in a subsequent article, from the fact that it is assumed without sufficient reason that the dissociations of the salts which are used to influence each other's solubility are the same.

The next paper bearing on this important subject is by Jones[4] who made a large number of careful determinations with most excellent apparatus, of the lowering of the freezing-point of very dilute salt-solutions. Several different salts were used, and their dissociation as calculated from his experiments, agree closely with those obtained by conductivity, and, consequently, differ from those found by Noyes.

For the sake of completeness it is necessary to state that Noyes[5] wrote a short reply to Arrhenius in which he calls attion to the latter's unwarranted assumptions, but admits that he is convinced that water is not dissociated sufficiently to account for the difference between theoretical and observed values of conductivity.

[1] Ztschr. phys. Chem., **6**, 241.
[2] *Ibid.* **11**, 391.
[3] Ann. der Phys. Pogg., **103**, 13.
[4] Ztschr. phys. Chem., **11**, 529.
[5] *Ibid.* **12**, 162.

The final and very satisfactory paper is by Noyes and Abbot.[1] In this, attention is called to the fact that the error which led to the discrepancies between results given in Noyes' earlier communications and those found by conductivity, was his assumption that thallous chloride is dissociated the same as the chlorides of the alkali metals. Neither this nor any other assumption is now made, but everything based on experiment as follows: Let m_o and m'_o be the solubilities of two salts in pure water, m and m' their respective solubilities when both are present in excess, α_o, α'_o, α and α' the corresponding values of dissociation. We then have at once, for binary electrolytes, $m_o(1-\alpha_o)=m(1-\alpha)$, $m'_o(1-\alpha'_o)=m'(1-\alpha')$, $m_o{}^2\alpha_o{}^2=m\alpha(m\alpha+m'\alpha')$ and $m'_o{}^2\alpha'_o{}^2=m'\alpha'(m\alpha+m'\alpha')$. These four equations involving only four unknowns, α_o, α'_o, α and α' enable us to find the value of any one of them in terms of known quantities. Values of dissociation determined in this way agree almost exactly with those found by conductivity and lowering of the freezing-point, thus giving further support to Nernst's solution law, and also showing that the so-called dissociation-constant—ratio of undissociated molecules in solution to the product of the ions—is really not a constant but a variable that increases with increase of dilution, though why this should be so no one has yet satisfactorily answered.

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[1] *Ibid.*, **16**, 125.